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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re Application of		:	PATENT
	Michael KAMLEITER et al.	:	Confirmation No. 4931
Serial No.:	10/582,349	:	Art Unit: 1777
Filed:	January 8, 2008	:	Examiner: K. S. Menon
For:	METHOD FOR PRODUCTION OF TUBULAR MEMBRANES	:	Appeal No. __________

BRIEF ON APPEAL

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APPELLANTS' BRIEF
ON APPEAL UNDER 37 C.F.R. §41.37

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

For the appeal to the Board of Patent Appeals and Interferences from the decision dated October 28, 2010 of the Primary Examiner twice and finally rejecting claims 10-14, 16-26 and 28-33 in connection with the above-identified application, Applicants-Appellants submit the following brief in accordance with 37 CFR §41.37.

1. Real Party in Interest

The inventor, Wilhelm N. Gudernatsch, assigned his entire rights, titles and interests in the patent application to Poromedia GmbH of Stuttgart, Germany. Poromedia GmbH also owned all rights, titles and interest of inventor Michael Kamleiter, who refused to sign the appropriate

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documents. Poromedia GmbH assigned its entire rights, titles and interest in the patent application to X-Flow B.V. of Enschede, The Netherlands.

2. Related Appeals and Interferences

There are no other related appeals or interferences known to Appellant, Appellant's legal representative, or assignees, which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending Appeal.

3. Status of Claims

Claims 1-9 are cancelled. Claims 10-14, 16-26 and 28-33 are pending, are rejected, and are on appeal. Claims 15 and 27 are objected to as being dependent on a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims, and are not on appeal.

4. Status of Amendments

Subsequent to the October 28, 2010 Office Action containing the final rejection, a January 28, 2011 Response and a February 9, 2011 Reply were filed without amending the claims.

5. Summary of Claimed Subject Matter

Independent claim 10 covers a method of producing membranes comprising constructing a tubular body 10 having a longitudinal axis from a plurality of threads 12 such that some of the threads 12 are tied substantially firmly together along fillet-shaped connecting lines 14 with continuous longitudinal threads parallel to the longitudinal axis (FIG. 1; p. 5, lines 19-22 and 24-

27). Between the fillet-shaped connecting lines 14, at least some of the threads 12 are formed as planar transverse connections 16 between mutually adjacent ones of the fillet-shaped connecting lines (FIG. 1; p. 5, lines 22-23). A predefinable membrane material 18 is applied to the tubular body (FIG. 1; p. 5, lines 23-24).

Independent claim 23 covers a tubular membrane comprising a tubular body 10 having a longitudinal axis constructed from a plurality of threads 12 with some of the threads 12 being tied substantially firmly together along fillet-shaped connecting lines 14 with continuous longitudinal threads parallel to the longitudinal axis (FIG. 1; p. 5, lines 19-22 and 24-27). Some of the threads 12 form planar transverse connections 16 extending between mutually adjacent connecting lines (FIG. 1; p. 5, lines 22-23). A predefinable membrane material 18 is applied to the tubular body (FIG. 1; p. 5, lines 23-24).

By forming the membranes in this manner, optimal tubular membranes can be obtained at a high production rate and at low cost. Moreover, these tubular membranes will not suffer undesired stretching effects. The production method is particularly enhanced by membranes being produced continuously, and thus, inexpensively.

6. <u>Grounds for Rejection to be Reviewed Upon Appeal</u>

Claims 16 and 24 stand rejected under 35 U.S.C. § 112, first paragraph, as failing to be based on an enabling disclosure.

Claims 10-14, 16-26 and 28-33 stand rejected under 35 U.S.C. § 103 as being unpatentable over U.S. Patent No. 5,034,129 to Ten Hove in view of U.S. Patent No. 6,454,942 to Shintani, with further evidence from U.S. Patent Publication Nos. 2002/0046970 to Murase and 2003/0098275 to Mahendran.

Claims 10-14, 16-26 and 28-33 stand rejected under 35 U.S.C. § 103 as being unpatentable over U.S. Patent No. 5,359,735 to Stockwell with further evidence from the Shintani patent and the Murase and Mahendran publications.

Claims 10-14, 16-26 and 28-33 stand rejected under 35 U.S.C. § 102 as being anticipated by the Stockwell patent.

7. Arguments

A. Rejections Under 35 U.S.C. § 112, First Paragraph

1. The Rejections

Claims 16 and 24 stand rejected under 35 U.S.C. §112, first paragraph, on the ground that the specification does not provide adequate information to enable the invention to be made and used in connection with graphite powder and activated charcoal. The specification is only found to be enabling for various fibers and filaments.

2. Specification Provides Adequate Information When Claims Properly Interpreted

When claims 16 and 24 are properly interpreted to recite monofilaments or multifilament at least partially of or with "graphite powder" or "activated charcoal," the patents listed in Appendix B demonstrate that a person skilled in the pertinent art would be able to make and use the subject matter of these claims based on the specification of this application without undue experimentation.

Page 5, line 34, of the substitute specification specifically refers to filaments of "graphite powder", "activated charcoal" and "ones constructed of powder". Obtaining such threads of graphite powder and activated charcoal are known. For example, U.S. Patent No. 7,695,026, at col. 10, lines 35-40, refers to functional powder carried in a carrier such as synthetic fibers,

where activated charcoal is specifically referenced as one of the powders. This patent supports the disclosure since it adequately shows knowledge by others as of its May 13, 2004 effective filing date. This date is before the September 17, 2004 International and effective U.S. filing date of this application. See M.P.E.P. § 2164.05(a). Additionally, U.S. Patent No. 4,740,434 (e.g., at column 2, lines 38-45) discloses "activated charcoal fibers"; U.S. Patent No. 5,595,659 (column 4, lines 22-24) discloses fibers with "activated charcoal"; U.S. Patent No. 5,071,070 (e.g., at column 2, lines 26-27) discloses a "graphite short fiber"; and U.S. Patent No. 5,134,030 (e.g., in claim 38) refers to "fibers impregnated with . . . graphite powder." These additional patents clearly show that one skilled in the art could make and use fibers of activated charcoal and of graphite powder, as claimed, particularly since "fibers" would be recognized as adequate support for and the equivalent of threads, monofilaments and multifilaments that are fibers. The specification need not disclose this information that is known in the prior art. Lindemann Maschinenfabrik GmbH v. American Hoist & Derrick, 730 F.2d 1452, 1463, 221 USPQ 481, 489 (Fed. Cir. 1984).

This rejection also appears to involve a misinterpretation of the claims in interpreting monofilaments or multifilaments of graphite powder and activated charcoal as being formed exclusively of those materials. However, the graphite powder and activated charcoal need only be a part of the monofilaments or multifilaments of the nature described in the above patents. The final rejection does not set forth the scope of the claims as required by M.P.E.P. 2164.04.

No evidence in the form of references or reasonable basis is supplied supporting the allegation that those threads are not known such that the rejection fails to comply with the requirements of M.P.E.P. §2164.04. In re Marzocchi, 439 F.2d 220, 224, 169 USPQ 367, 370

(C.C.P.A. 1971). Thus, the application adequately supports all claimed subject matter as required by 35 U.S.C. §112.

In view of the foregoing, claims 16 and 24 comply with 35 U.S.C. §112, and reversal of this rejection is requested.

B. Rejections over Ten Hove and Shintani Patents and Murase and Mahendran Publications

1. The Rejections

Claims 10-14, 16-26 and 28-33 stand rejected under 35 U.S.C. § 103 as being unpatentable over U.S. Patent No. 5,034,129 to Ten Hove in view of U.S. Patent No. 6,454,942 to Shintani, with further evidence from U.S. patent publication 2002/0046970 to Murase or U.S. patent publication 2003/0098275 to Mahendran. The Ten Hove patent, particularly relative to Fig. 4, is cited for a process of making a membrane having a woven or knitted tube 11 over a mandrel 8 and then another non-woven, woven or knitted tube 12 slipped over tube 11, with a woven or knitted tube allegedly being an alternative to the non-woven external tube 12. A membrane allegedly is applied to the inside of tube 11 (col. 4, lines 10-29), with the membrane material being polysulfone, PVdF and the fabric material being plastic or polyester. The forming of the membrane is allegedly disclosed by coating and then passing through a precipitation bath (col. 4, lines 34-36). The Shintani patent is cited for a tricot fabric as a membrane support having fillet-like connecting lines transversely linked by threads forming transverse connections. In support of the rejection, it is alleged that it would be obvious to use the Shintani structure for providing a tricot weave for tubes 11 and 12 of the Ten Hove structure. Additionally, a tricot weave is allegedly a knit weave produced by a crocheting device with hook needles with the fillet lines less permeable than the space between them and with the tricot being polyester or similar

polymer. The angle between adjacent transverse filaments is allegedly shown or obvious from the Shintani patent. The Ten Hove and Shintani patents in combination are alleged to teach a tubular membrane. The plastic materials are also allegedly taught by these two patents. The two cited patent publications are also apparently cited for teaching the use of other materials for the fibers.

2. Claim 10 is Patentably Distinguishable By Use of Continuous Longitudinal Threads Parallel to the Longitudinal Axis

Claim 10 is patentably distinguishable over the cited patents, particularly over the Shintani patent, by the continuous longitudinal threads parallel to the longitudinal axis. Relative to this feature, page 9 of the Office Action states that the ball 22 in Fig. 1 of this application is the best representation of the longitudinal thread in the specification which is alleged to be the equivalent of the knots shown in the figure of the Shintani patent. However, the longitudinal threads are best shown by the lines 14, not the balls 22, demonstrating that the Shintani knots are not the equivalent of the claimed longitudinal threads.

While the Ten Hove patent discloses a membrane assembly, admittedly, no details are provided therein regarding the knitted tubes 11 and 12. Particularly, neither of the Ten Hove knitted tubes are disclosed as being constructed of a tubular body having the specific thread arrangement recited in claim 10. Such deficiencies are not cured by the Shintani patent.

The Shintani patent discloses a liquid separation membrane module that does not appear to show it formed into a tubular body. Though Figs. 4 and 5 illustrate a spiral wound type liquid separation module using the channel material, that embodiment does not provide a tubular body in which the threads are constructed, as recited in the method of claim 10. Specifically, claim 10 recites that the fillet-shaped connecting lines have continuous longitudinal threads 14 parallel to

the longitudinal axis. No continuous longitudinal threads are provided in the knotted fillet lines alleged to be provided in the Shintani tricot fabric as clearly shown by the empty horizontal and vertical spaces between the knots of FIG. 1. Additionally, claim 10 recites forming at least some of the threads as planar transverse connections. The transverse connections allegedly present in the Shintani fabric are not shown to be planar.

Longitudinal tensile stretches arising during filtration are taken up by the continuous longitudinal threads along the fillet-shaped connecting lines. The stresses at the periphery are taken up safely by the transverse threads by way of the planar transverse connections. The forming of the features (particularly the continuous longitudinal threads) providing these advantages are <u>not</u> disclosed or rendered obvious by the Ten Hove and Shintani patents considered individually or in any obvious combination thereof. No disclosure in the Ten Hove or Shintani patent (particularly the Shintani knots) provides the method steps of forming this structure of the claims, and no analysis is provided to support the implicitly provided allegation of the February 7, 2011 Advisory Action.

The Murase and Mahendran publications are apparently cited solely relative to materials for the fibers and not for the subject matter of claim 10, and accordingly do not cure the deficiencies in the Ten Hove and Shintani patents.

Thus, claim 10 is patentably distinguishable over the Ten Hove and Shintani patents and the Murase and Mahendran publications.

3. <u>Claims Dependent Upon Claim 10</u>

Claims 11-14 and 16-22, being dependent upon claim 10, are also allowable for the above reasons. Moreover, these dependent claims recite additional features further distinguishing them over the cited patents and publications.

a. Claim 11

Claim 11 is further distinguishable by the specific crocheting steps. Such steps are not shown to be disclosed or obvious from the cited patents and publications.

b. Claim 12

Claim 12 is further distinguishable by the crocheting with passages and the connecting lines formed to be liquid tight or with a low flow rate. Those features are not shown to be disclosed or rendered obvious.

c. Claim 13

Claim 13 is further distinguishable by the use of the specific materials recited in this method.

d. Claim 14

Claim 14 is further distinguishable by the use of the specific materials recited in this method.

e. Claim 16

Claim 16 is further distinguishable by the specific threads recited therein that are not shown to be disclosed or rendered obvious by the cited patents and publications.

f. Claim 17

Claim 17 is further distinguishable by the specific 10°-70° angle between the threads of the transverse connections. Such angle is not shown to be disclosed or rendered obvious by the cited patents and publications. No reason or analysis supports the allegation of obviousness.

g. Claim 18

Claim 18 is further distinguishable by the approximately 30° angle between the threads of the threads of the transverse connections. That angle is not disclosed or rendered obvious by the

cited patents and publications. No evidence or analysis is provided to support the allegation of obviousness.

h. Claim 19

Claim 19 is further distinguishably by the use of at least three surfaces of the transverse connections in this method. These surfaces are not shown to be disclosed or rendered obvious in the applied citations.

i. Claim 20

Claim 20 is further distinguishable by the use of six surfaces in this method. This number of surfaces is not shown to be disclosed or rendered obvious by the applied citations.

j. Claim 21

Claim 21 is further distinguishable by the use of the specific membrane materials recited therein in this method.

k. Claim 22

Claim 22 is further distinguishable by the use of the specific membrane materials recited therein in this method.

4. Claim 23 is Patentably Distinguishable By Continuous Longitudinal Threads Parallel to the Longitudinal Axis

Claim 23 is patentably distinguishable over the cited patents, particularly over the Shintani patent, by the continuous longitudinal threads parallel to the longitudinal axis. Relative to this feature, page 9 of the Office Action states that the ball 22 in Fig. 1 of this application is the best representation of the longitudinal thread in the specification which is alleged to be the equivalent of the knots shown in the figure of the Shintani patent. However, the longitudinal

threads are best shown by the lines 14, not the balls 22, demonstrating that the Shintani knots are not the equivalent of the claimed longitudinal threads.

While the Ten Hove patent discloses a membrane assembly, admittedly, no details are provided therein regarding the knitted tubes 11 and 12. Particularly, neither of the Ten Hove knitted tubes are disclosed as being constructed of a tubular body having the specific thread arrangement recited in claim 23. Such deficiencies are not cured by the Shintani patent.

The Shintani patent discloses a liquid separation membrane module that does not appear to show it formed into a tubular body. Though Figs. 4 and 5 illustrate a spiral wound type liquid separation module using the channel material, that embodiment does not provide a tubular body in which the threads are constructed, as recited in the tubular membrane of claim 23. Specifically, claim 23 recites that the fillet-shaped connecting lines have continuous longitudinal threads 14 parallel to the longitudinal axis. No continuous longitudinal threads are provided in the knotted fillet lines alleged to be provided in the Shintani tricot fabric as clearly shown by the empty horizontal and vertical spaces between the knots of FIG. 1. Additionally, claim 23 recites at least some of the threads as planar transverse connections. The transverse connections allegedly present in the Shintani fabric are not shown to be planar.

Longitudinal tensile stretches arising during filtration are taken up by the continuous longitudinal threads along the fillet-shaped connecting lines. The stresses at the periphery are taken up safely by the transverse threads by way of the planar transverse connections. The features (particularly the continuous longitudinal threads) providing these advantages are clearly not disclosed or rendered obvious by the Ten Hove and Shintani patents considered individually or in any obvious combination there. No disclosure in the Ten Hove or Shintani patent

(particularly the Shintani knots) provides this structure of the claims, and no analysis is provided to support the implicitly provided allegation of the February 7, 2011 Advisory Action.

The Murase and Mahendran publications are apparently cited solely relative to materials for the fibers and not for the subject matter of claim 23, and accordingly do not cure the deficiencies in the Ten Hove and Shintani patents.

Thus, claim 23 is patentably distinguishable over the Ten Hove and Shintani patents and the Murase and Mahendran publications.

5. Claims Dependent Upon Claim 23

Claims 24-26 and 28-33, being dependent upon claim 23, are also allowable for the above reasons. Moreover, these dependent claims recite additional features further distinguishing them over the cited patents and publications.

a. Claim 24

Claim 24 is further distinguishable by the passages 20 extending through the transverse connections 16 for allowing a high rate of fluid to flow therethrough and the fluid light or low flow rate through the connecting lines 14. Such structures are not shown to be disclosed or obvious from the cited patents or publications.

b. Claim 25

Claim 25 is further distinguishable by the use of the specific materials for the threads recited therein.

c. Claim 26

Claim 26 is further distinguishable by the use of the specific materials for the threads recited therein.

d. Claim 28

Claim 28 is further distinguishable by the specific threads recited therein that are not shown to be disclosed or rendered obvious by the cited patents and publications.

e. Claim 29

Claim 29 is further distinguishable by the specific 10°-70° angle between the threads of the transverse connections. Such angle is not shown to be disclosed or rendered obvious by the cited patents and publications. No reason or analysis supports the allegation of obviousness.

f. Claim 30

Claim 30 is further distinguishable by the approximately 30° angle between the threads of the threads of the transverse connections. That angle is not disclosed or rendered obvious by the cited patents and publications. No evidence or analysis is provided to support the allegation of obviousness.

g. Claim 31

Claim 31 is further distinguishably by the use of at least three surfaces of the transverse connections in this method. These surfaces are not shown to be disclosed or rendered obvious in the applied citations.

h. Claim 32

Claim 32 is further distinguishable by the use of six surfaces in this method. This number of surfaces is not shown to be disclosed or rendered obvious by the applied citations.

i. Claim 33

Claim 33 is further distinguishable by the use of the specific membrane materials recited therein in this method.

C. Rejections Over Stockwell and Shintani Patents and Murase and Mahendran Publications

1. The Rejections

Claims 10-14, 16-26 and 28-33 also stand rejected under 35 U.S.C. § 103 as being unpatentable over the Stockwell patent with further evidence from the Shintani patent and the Murase and Mahendran patent publications. The Stockwell patent is cited for teaching a method coating a breathable material over a circular knit fabric of a tricot weave (col. 3, lines 64-69). Although the Stockwell patent is stated as not having the details of the tricot weave, such details are allegedly taught by the Shintani patent in the same manner as the above rejection. The materials for fibers are alleged as being obvious, as allegedly taught by the Murase and Mahendran publications.

2. Claim 10 is Patentably Distinguishable By Continuous Longitudinal Threads Parallel to the Longitudinal Axis

The rejection based on the Stockwell patent in view of the Shintani patent suffers the same deficiencies. Admittedly, the Stockwell patent does not disclose the details of the tricot weave necessary to meet the claim limitations.

Claim 10 is patentably distinguishable over the cited patents, particularly over the Shintani patent, by the continuous longitudinal threads parallel to the longitudinal axis. Relative to this feature, page 9 of the Office Action states that the ball 22 in Fig. 1 of this application is the best representation of the longitudinal thread in the specification which is alleged to be the equivalent of the knots shown in the figure of the Shintani patent. However, the longitudinal threads are best shown by the lines 14, not the balls 22, demonstrating that the Shintani knots are not the equivalent of the claimed longitudinal threads.

While the Stockwell patent discloses a coated tricot fabric, admittedly, no details are provided therein regarding that fabric. Particularly, the Stockwell fabric is not disclosed as being constructed of a tubular body having the specific thread arrangement recited in claim 10. Such deficiencies are not cured by the Shintani patent.

The Shintani patent discloses a liquid separation membrane module that does not appear to show it formed into a tubular body. Though Figs. 4 and 5 illustrate a spiral wound type liquid separation module using the channel material, that embodiment does not provide a tubular body in which the threads are constructed, as recited in the method of claim 23. Specifically, claim 23 recites that the fillet-shaped connecting lines have continuous longitudinal threads 14 parallel to the longitudinal axis. No continuous longitudinal threads are provided in the knotted fillet lines alleged to be provided in the Shintani tricot fabric as clearly shown by the empty horizontal and vertical spaces between the knots of FIG. 1. Additionally, claim 23 recites forming at least some of the threads as planar transverse connections. The transverse connections allegedly present in the Shintani fabric are not shown to be planar.

Longitudinal tensile stretches arising during filtration are taken up by the continuous longitudinal threads along the fillet-shaped connecting lines. The stresses at the periphery are taken up safely by the transverse threads by way of the planar transverse connections. The forming of the features (particularly the continuous longitudinal threads) providing these advantages are clearly not disclosed or rendered obvious by the Stockwell and Shintani patents considered individually or in any obvious combination there. No disclosure in the Stockwell or Shintani patent (particularly the Shintani knots) provides the method steps of forming this structure of the claims, and no analysis is provided to support the implicitly provided allegation of the February 7, 2011 Advisory Action.

The Murase and Mahendran publications are apparently cited solely relative to materials for the fibers and not for the subject matter of claim 10, and accordingly do not cure the deficiencies in the Ten Hove and Shintani patents.

Thus, claim 10 is patentably distinguishable over the Stockwell and Shintani patents and the Murase and Mahendran publications.

3. Claims Dependent Upon Claim 10

Claims 11-14, 16 and 22, being dependent upon claim 10, are also allowable for the above reasons. Moreover, these dependent claims recite additional features further distinguishing them over the cited patents and publications.

a. Claim 11

Claim 11 is further distinguishable by the specific crocheting steps. Such steps are not shown to be disclosed or obvious from the cited patents and publications.

b. Claim 12

Claim 12 is further distinguishable by the crocheting with passages and the connecting lines formed to be liquid tight or with a low flow rate. Those features are not shown to be disclosed or rendered obvious.

c. Claim 13

Claim 13 is further distinguishable by the use of the specific materials recited in this method.

d. Claim 14

Claim 14 is further distinguishable by the use of the specific materials recited in this method.

e. Claim 16

Claim 16 is further distinguishable by the specific threads recited therein that are not shown to be disclosed or rendered obvious by the cited patents and publications.

f. Claim 17

Claim 17 is further distinguishable by the specific 10°-70° angle between the threads of the transverse connections. Such angle is not shown to be disclosed or rendered obvious by the cited patents and publications. No reason or analysis supports the allegation of obviousness.

g. Claim 18

Claim 18 is further distinguishable by the approximately 30° angle between the threads of the threads of the transverse connections. That angle is not disclosed or rendered obvious by the cited patents and publications. No evidence or analysis is provided to support the allegation of obviousness.

h. Claim 19

Claim 19 is further distinguishably by the use of at least three surfaces of the transverse connections in this method. These surfaces are not shown to be disclosed or rendered obvious in the applied citations.

i. Claim 20

Claim 20 is further distinguishable by the use of six surfaces in this method. This number of surfaces is not shown to be disclosed or rendered obvious by the applied citations.

j. Claim 21

Claim 21 is further distinguishable by the use of the specific membrane materials recited therein in this method.

k. Claim 22

Claim 22 is further distinguishable by the use of the specific membrane materials recited therein in this method.

4. Claim 23 is Patentably Distinguishable By Continuous Longitudinal Threads Parallel to the Longitudinal Axis

Claim 23 is patentably distinguishable over the cited patents, particularly over the Shintani patent, by the continuous longitudinal threads parallel to the longitudinal axis. Relative to this feature, page 9 of the Office Action states that the ball 22 in Fig. 1 of this application is the best representation of the longitudinal thread in the specification which is alleged to be the equivalent of the knots shown in the figure of the Shintani patent. However, the longitudinal threads are best shown by the lines 14, not the balls 22, demonstrating that the Shintani knots are not the equivalent of the claimed longitudinal threads.

While the Stockwell patent discloses a coated tricot fabric, admittedly, no details are provided therein regarding that fabric. Particularly, the Stockwell fabric is disclosed as being constructed of a tubular body having the specific thread arrangement recited in claim 23. Such deficiencies are not cured by the Shintani patent.

The Shintani patent discloses a liquid separation membrane module that does not appear to show it formed into a tubular body. Though Figs. 4 and 5 illustrate a spiral wound type liquid separation module using the channel material, that embodiment does not provide a tubular body in which the threads are constructed, as recited in the tubular membrane of claim 23. Specifically, claim 23 recites that the fillet-shaped connecting lines have continuous longitudinal threads 14 parallel to the longitudinal axis. No continuous longitudinal threads are provided in the knotted fillet lines alleged to be provided in the Shintani tricot fabric as clearly shown by the

empty horizontal and vertical spaces between the knots of FIG. 1. Additionally, claim 23 recites at least some of the threads as planar transverse connections. The transverse connections allegedly present in the Shintani fabric are not shown to be planar.

Longitudinal tensile stretches arising during filtration are taken up by the continuous longitudinal threads along the fillet-shaped connecting lines. The stresses at the periphery are taken up safely by the transverse threads by way of the planar transverse connections. The features (particularly the continuous longitudinal threads) providing these advantages are clearly not disclosed or rendered obvious by the Stockwell and Shintani patents considered individually or in any obvious combination there. No disclosure in the Stockwell or Shintani patent (particularly the Shintani knots) provides this structure of the claims, and no analysis is provided to support the implicitly provided allegation of the February 7, 2011 Advisory Action.

The Murase and Mahendran publications are apparently cited solely relative to materials for the fibers and not for the subject matter of claim 23, and accordingly do not cure the deficiencies in the Ten Hove and Shintani patents.

Thus, claim 23 is patentably distinguishable over the Stockwell and Shintani patents and the Murase and Mahendran publications.

5. Claims Dependent Upon Claim 23

Claims 24-26 and 28-33, being dependent upon claim 23, are also allowable for the above reasons. Moreover, these dependent claims recite additional features further distinguishing them over the cited patents and publications.

a. Claim 24

Claim 24 is further distinguishable by the passages 20 extending through the transverse connections 16 for allowing a high rate of fluid to flow therethrough and the fluid light or low

flow rate through the connecting lines 14. Such structures are not shown to be disclosed or obvious from the cited patents or publications.

b. Claim 25

Claim 25 is further distinguishable by the use of the specific materials for the threads recited therein.

c. Claim 26

Claim 26 is further distinguishable by the use of the specific materials for the threads recited therein.

d. Claim 28

Claim 28 is further distinguishable by the specific threads recited therein that are not shown to be disclosed or rendered obvious by the cited patents and publications.

e. Claim 29

Claim 29 is further distinguishable by the specific 10°-70° angle between the threads of the transverse connections. Such angle is not shown to be disclosed or rendered obvious by the cited patents and publications. No reason or analysis supports the allegation of obviousness.

f. Claim 30

Claim 30 is further distinguishable by the approximately 30° angle between the threads of the threads of the transverse connections. That angle is not disclosed or rendered obvious by the cited patents and publications. No evidence or analysis is provided to support the allegation of obviousness.

g. Claim 31

Claim 31 is further distinguishably by the use of at least three surfaces of the transverse connections in this method. These surfaces are not shown to be disclosed or rendered obvious in the applied citations.

h. Claim 32

Claim 32 is further distinguishable by the use of six surfaces in this method. This number of surfaces is not shown to be disclosed or rendered obvious by the applied citations.

i. Claim 33

Claim 33 is further distinguishable by the use of the specific membrane materials recited therein in this method.

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When no reference discloses a feature of a claim relied on to distinguish the prior art, there can be no suggestion to modify the prior art to contain that feature. In re Civitello, 339 F.2d 243, 144 USPQ 10 (C.C.P.A. 1964). As stated in W. L. Gore & Associates, Inc. v. Garlock, Inc., 721 F.2d 1540, 1551, 220 USPQ 303, 311 (Fed. Cir. 1983), there must be something in the teachings of the cited patents to suggest or to provide a reason to one skilled in the art that the claimed invention would be obvious.

Despite the simple concept of the invention, the Examiner has the burden of finding "the specific understanding or principle within the knowledge of a skilled artisan that would have motivated one with no knowledge of [the] invention to make the combination in the manner claimed." See In re Werner Kotzab, 217 F.3d 1365, 1371, 55 USPQ 2d 1313, 1318 (Fed. Cir. 2000). Here, the necessary factual findings are missing, rendering the rejection untenable.

The Examiner, in this situation has not pointed to any specific principle or motivation in the prior art that would lead one skilled in the art to arrive at the invention as claimed. "[P]articular findings must be made as to the reason the skilled artisan, with no knowledge of the claimed invention, would have selected these components for combination in the manner claimed." In re Werner Kotzab, 217 F.3d at 1371, 55 USPQ 2d at 1318. If no particular finding can be made as to the reason one skilled in the art would have used the features of the Shintani fabric in the Ten Hove or Stockwell device to produce the claimed invention, the Examiner cannot properly hold the claimed invention obvious.

The Examiner is using the Examiner's knowledge of the invention, in hindsight, to conclude improperly that one skilled in the art would have found it obvious to make the proposed combinations and modifications. However, such "hindsight reconstruction" is impermissible in reaching a finding of obviousness. See, e.g., W. L. Gore & Assocs., Inc. v. Garlock, Inc., 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983).

D. Rejection Over Stockwell Patent Alone

1. The Rejection

Claims 10-14, 16-26 and 28-33 stand rejected under 35 U.S.C. § 102 as being anticipated by U.S. Patent No. 5,359,735 to Stockwell. The Stockwell patent is cited as disclosing making "a coating of breathable material (a semi-permeably membrane) over a circular fabric – a tube of kit fabric," where the knit is allegedly a tricot weave based on column 3, lines 64-69. This disclosure is alleged to anticipate the subject matter of the claims.

2. Claims Not Anticipated

In view of the lack of any specific comparison of the Stockwell patent, and the claims on appeal and in view of the above arguments, applicants submit that the rejection under 35 U.S.C.

§ 102 is untenable and request reversal thereof. Mere reference to a tricot weave does <u>not</u> establish that all of the claimed subject matter of each claim on appeal is adequately disclosed in the Stockwell patent.

To support an anticipation rejection, all elements of the claim must be found in a single reference. <u>In re Royka et al.</u>, 490 F.2d 981, 984, 180 USPQ 580, 582 (CCPA 1974). Rejections under 35 U.S.C. § 102 are proper only when the claimed subject matter is identically disclosed or described in the prior art. <u>In re Marshall</u>, 578 F.2d 301, 304, 198 USPQ 344, 346 (CCPA 1978). Since all elements of any pending claims are not shown to be identically disclosed or described in the Stockwell patent, the rejection under 35 U.S.C. § 102 is untenable.

8. <u>Conclusion</u>

In view of the foregoing, the rejections of claims 16 and 24 under 35 U.S.C. §112 and the rejections of claims 10-14, 16-26 and 28-33 under 35 U.S.C. §102 or §103 are untenable, and a decision reversing those rejections is requested.

Respectfully submitted,

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Reg. No. 28,770

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Dated: April 22, 2011

APPENDIX A – COPY OF CLAIMS ON APPEAL

10. A method for producing membranes, comprising the steps of:

constructing a tubular body having a longitudinal axis from a plurality of threads such that some of the threads are tied substantially firmly together along fillet-shaped connecting lines with continuous longitudinal threads parallel to the longitudinal axis;

between the fillet-shaped connecting lines, forming at least some of the threads as planar transverse connections between mutually adjacent ones of the fillet-shaped connecting lines; and

applying a predefinable membrane material to the tubular body.

11. A method according to claim 10 wherein

the tubular body is constructed by a crocheting device, with each inserted thread being assigned a separate and respective hooked needle or crochet needle.

12. A method according to claim 11 wherein

the tubular body is constructed by crocheting with passages being formed between individual ones of the transverse connections for allowing liquid to pass through at high flow rates; and

the fillet-shaped connecting lines are formed liquid tight or formed to allow liquid to pass only at a low flow rate.

13. A method according to claim 10 wherein

the threads are monofilaments or multifilaments of synthetic materials selected from the group consisting of polyester, polyaramide, other polymers, carbon and Kevlar.

14. A method according to claim 10 wherein

the threads are monofilaments or multifilaments of metal selected from the group consisting of nickel, platinum, palladium, gold, silver and stainless steel.

16. A method according to claim 10 wherein

the threads are monofilaments or multifilaments of materials selected from the group consisting of glass fibers, graphite powder and activated charcoal.

17. A method according to claim 10 wherein

adjacent transverse connections are arranged between two connecting lines enclosing an angle therebetween of 10° to 70°.

18. A method according to claim 17 wherein

the angle is approximately 30°.

19. A method according to claim 10 wherein

the tubular body is constructed with at least three connecting lines and with at least three surfaces of transverse connections on which the membrane material is applied.

20. A method according to claim 10 wherein

the tubular body is constructed with at least six connecting lines and with at least six surfaces of transverse connections on which the membrane material is applied.

21. A method according to claim 10 wherein

the tubular body is coated with a membrane-activated substance by being guided through a precipitation bath, with the membrane-activatable substance being converted into a microporous membrane layer.

22. A method according to claim 10 wherein

the membrane material is a synthetic material selected from the group consisting of polyethersulfone, polysulfane, polyacrylonitrite and polyvinylidene fluoride.

23. A tubular membrane, comprising:

a tubular body having a longitudinal axis construction from a plurality of threads with some of the threads being tied substantially firmly together along fillet-shaped connecting lines having continuous longitudinal threads parallel to the longitudinal axis and with some of the threads forming planar transverse connections extending between mutually adjacent connecting lines; and

a predefinable membrane material applied on the tubular body.

24. A tubular membrane according to claim 23 wherein

passages extend between individual ones of the transverse connections for allowing liquid to pass through at high flow rates; and

the fillet-shaped connecting lines are liquid tight or allow to pass only at low flow rates.

25. A tubular membrane according to claim 23 wherein

the threads are monofilaments or multifilaments of synthetic materials selected from the group consisting of polyester, polyaramide, other polymers, carbon and Kevlar.

26. A tubular membrane according to claim 23 wherein

the threads are monofilaments or multifilaments of metal selected from the group consisting of nickel, platinum, palladium, gold, silver and stainless steel.

28. A tubular membrane according to claim 23 wherein

the threads are monofilaments or multifilaments of materials selected from the group consisting of cellulose acetate, glass fibers, graphite powder and activated charcoal.

29. A tubular membrane according to claim 23 wherein

adjacent transverse connections are arranged between two connecting lines enclosing an angle therebetween of 10° to 70°.

30. A tubular membrane according to claim 29 wherein

the angle is approximately 30°.

31. A tubular membrane according to claim 25 wherein

the tubular body is constructed with at least three connecting lines and with at least three surfaces of transverse connections on which the membrane material is applied.

32. A tubular membrane according to claim 25 wherein

the tubular body is constructed with at least six connecting lines and with at least six surfaces of transverse connections on which the membrane material is applied.

33. A tubular membrane according to claim 25 wherein

the membrane material is a synthetic material selected from the group consisting of polyethersulfone, polysulfane, polyacrylonitrite and polyvinylidene fluoride.

APPENDIX B – EVIDENCE

Attached are copies of the following U.S. patents entered by the Examiner in the February 16, 2011 Advisory Action and relied upon by the appellants in this appeal:

7,695,206

4,740,434

5,595,659

5,071,700

5,134,030

US007695026B2

(12) United States Patent
Okamoto et al.

(10) **Patent No.: US 7,695,026 B2**
(45) **Date of Patent: *Apr. 13, 2010**

(54) **TUBE DEVICE, AND PIPING SYSTEM INCLUDING THE TUBE DEVICE**

(75) Inventors: **Yutaka Okamoto**, Sanda (JP); **Tatsuya Fujii**, Sanda (JP)

(73) Assignee: **Nippon Pillar Packing Co., Ltd.**, Osaka (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **11/938,804**

(22) Filed: **Nov. 13, 2007**

(65) **Prior Publication Data**

US 2008/0136177 A1 Jun. 12, 2008

Related U.S. Application Data

(62) Division of application No. 10/844,881, filed on May 13, 2004, now Pat. No. 7,314,239.

(30) **Foreign Application Priority Data**

May 16, 2003 (JP) 2003-139140
May 16, 2003 (JP) 2003-139166
May 16, 2003 (JP) 2003-139222

(51) **Int. Cl.**
F16L 25/00 (2006.01)

(52) **U.S. Cl.** **285/331**; 285/332; 285/332.1

(58) **Field of Classification Search** 285/179, 285/246–247, 322, 331, 332, 332.1
See application file for complete search history.

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(Continued)

Primary Examiner—Aaron M Dunwoody
Assistant Examiner—Fannie Kee
(74) *Attorney, Agent, or Firm*—Panitch Schwarze Belisario & Nadel LLP

(57) **ABSTRACT**

A tube includes a casing made of a fluororesin. The casing surrounds a fluid tube and lid members, each made of a fluororesin and include a receiving portion for receiving one end portion of the tube. At least one sealing face is disposed in the receiving portion. Union nuts, made of a fluororesin, are fitted onto the end portion of the tube and screwed to one end portion of one of the lid members. A sealing portion is formed by fastening the union nuts to the end portions of the lid members to press the tube from the outside of the tube. A device element such as a filter member is placed in the casing.

5 Claims, 20 Drawing Sheets

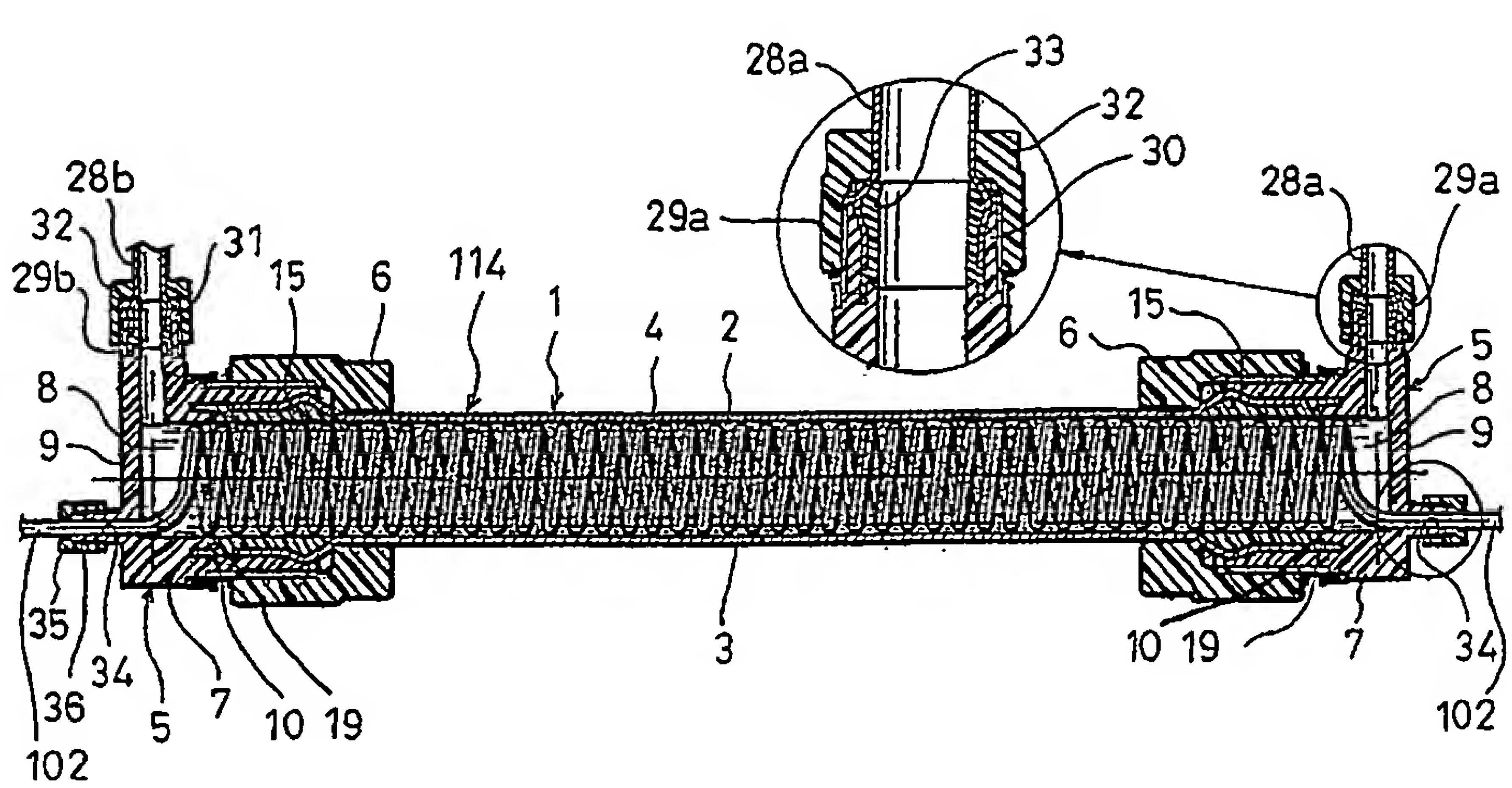

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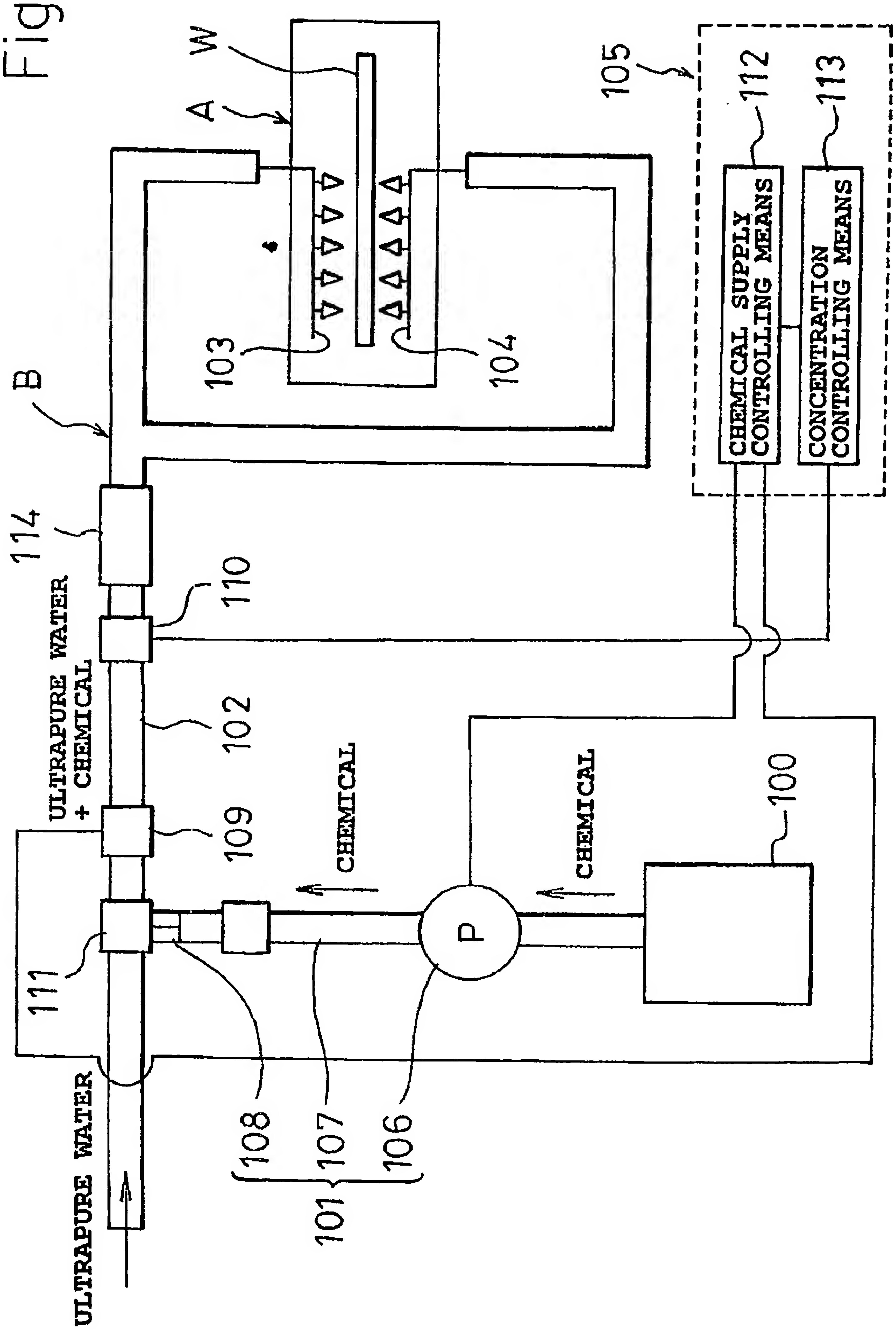
Fig. 1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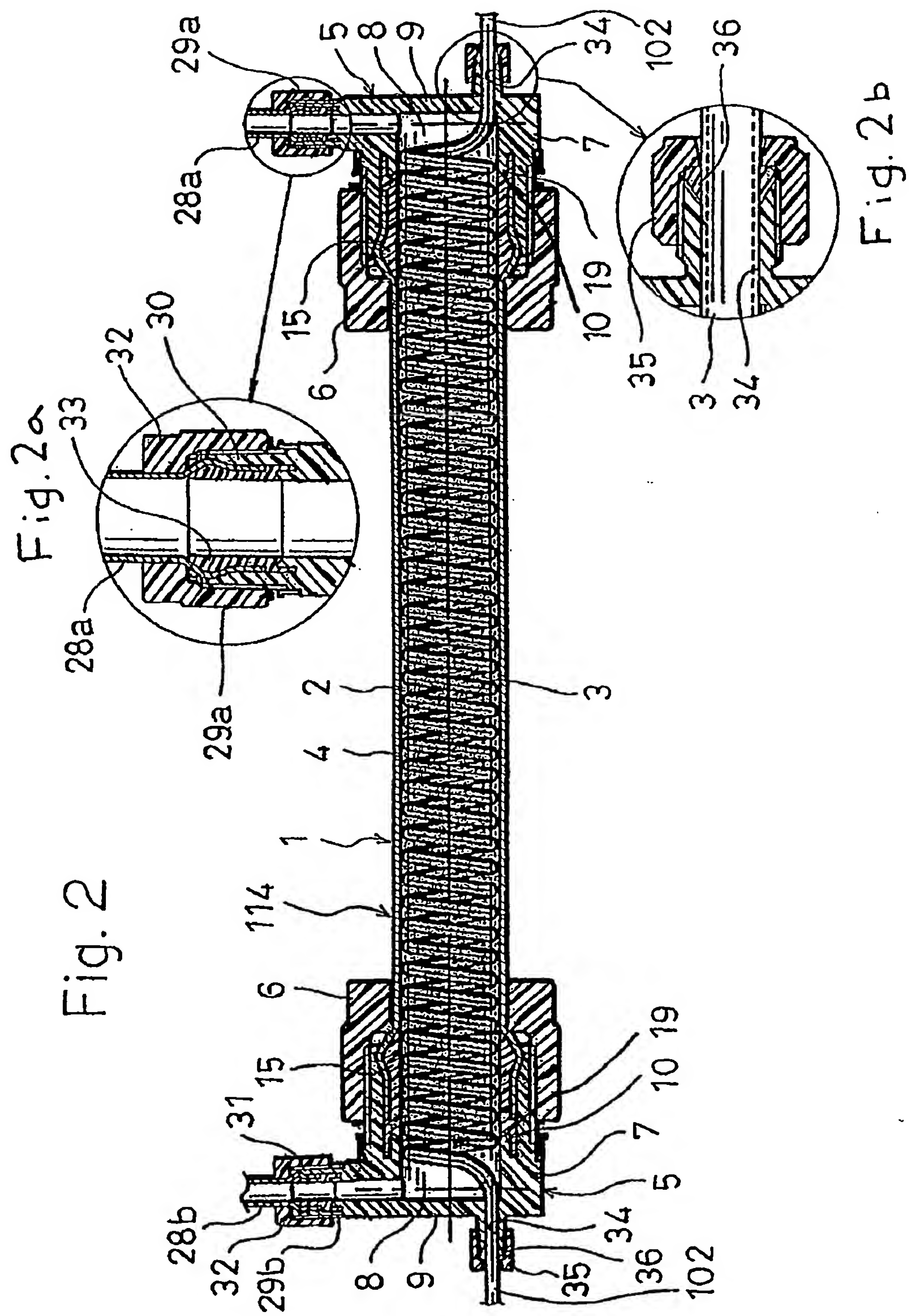
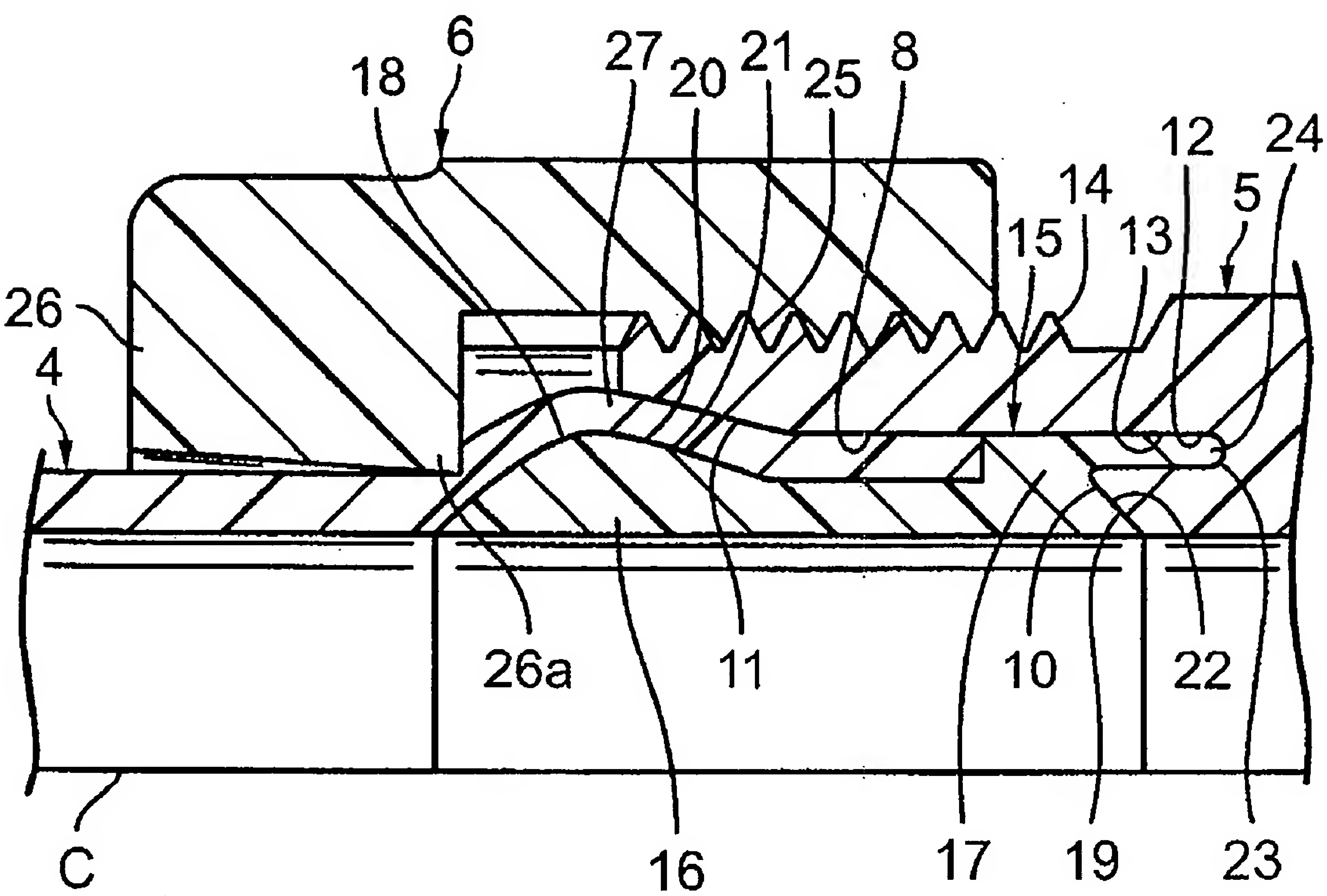


Fig. 2

Fig. 2a

Fig. 2b

Fig. 3



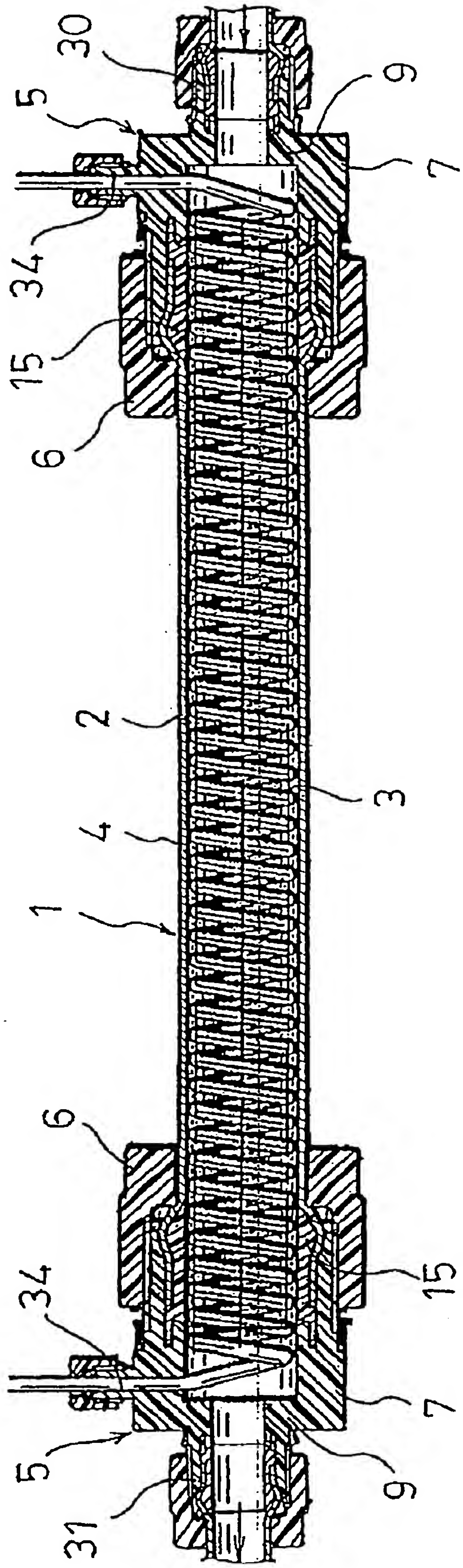


Fig. 4

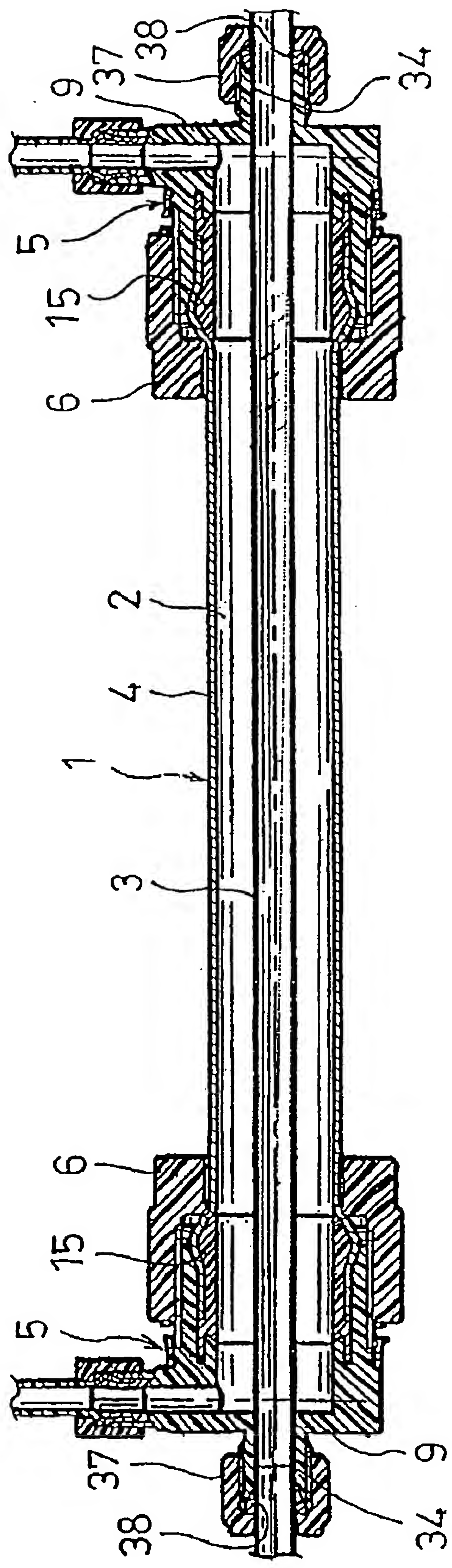


Fig. 5

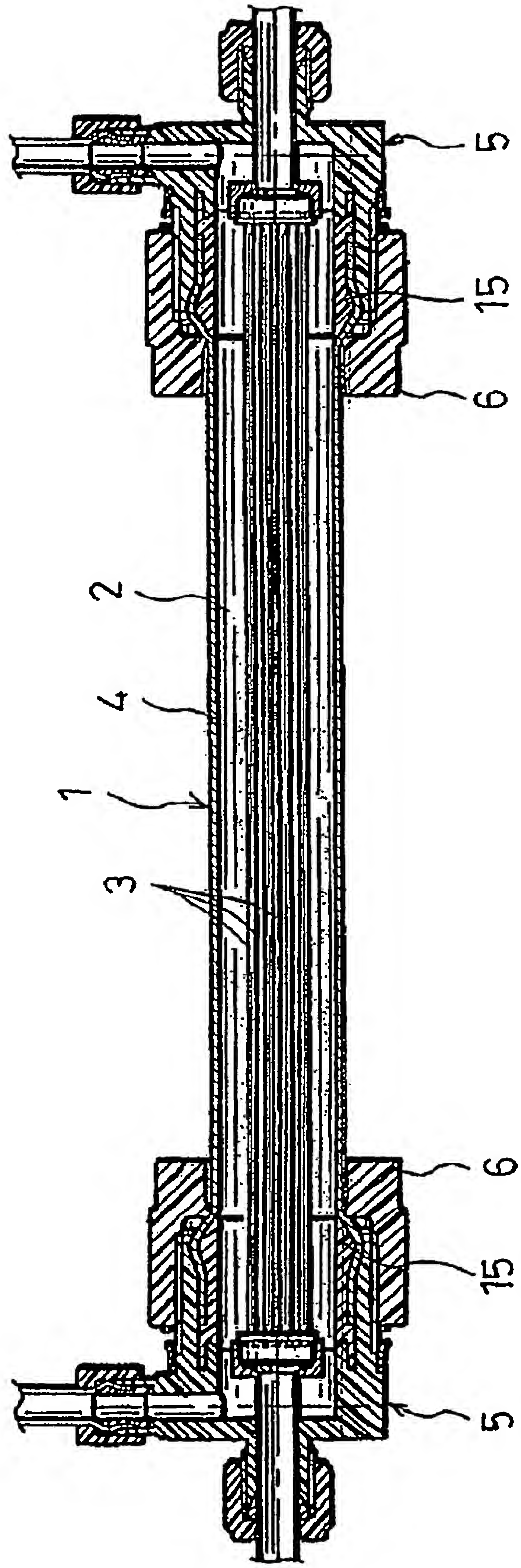


Fig. 6

Fig. 7

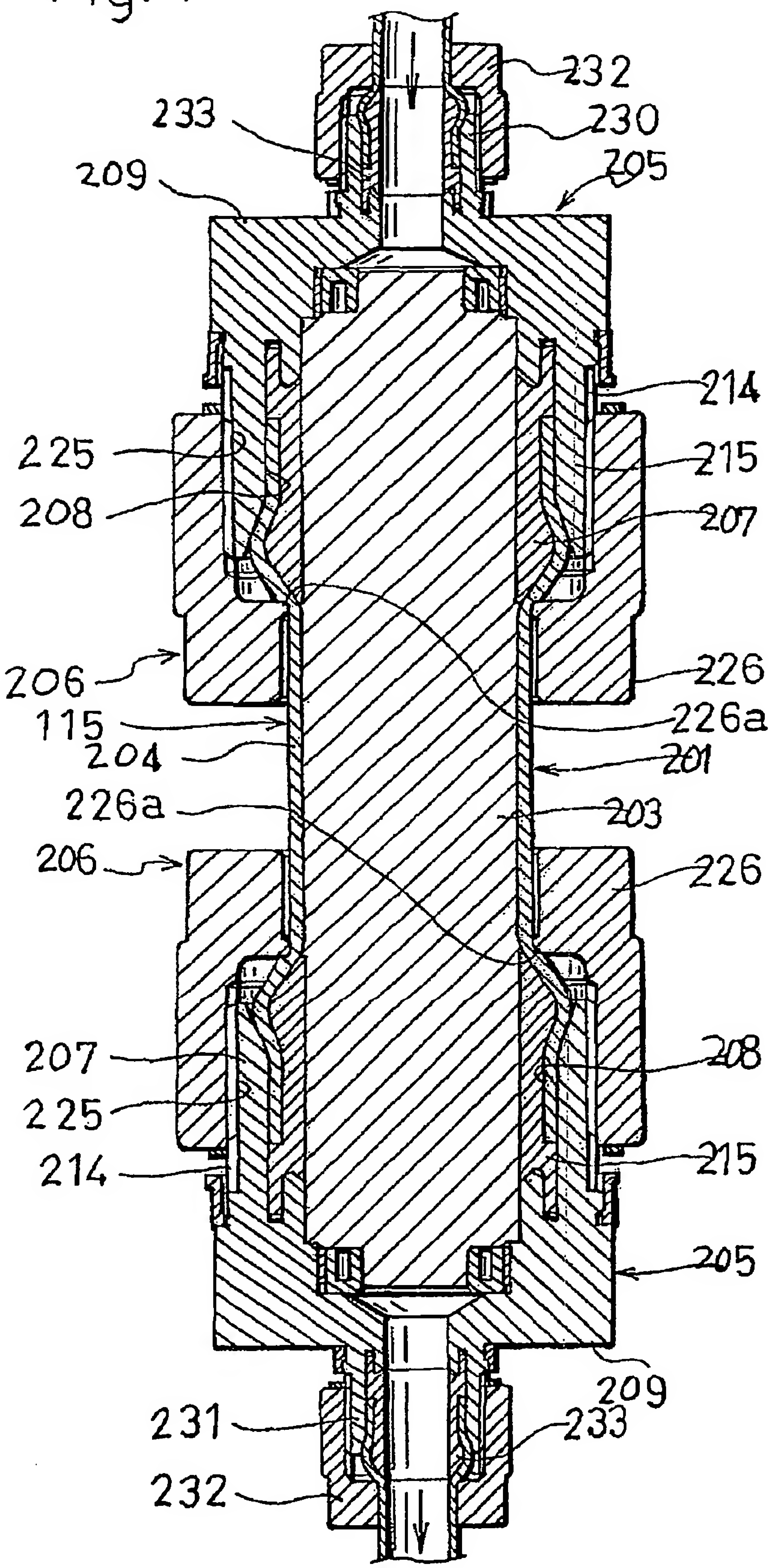

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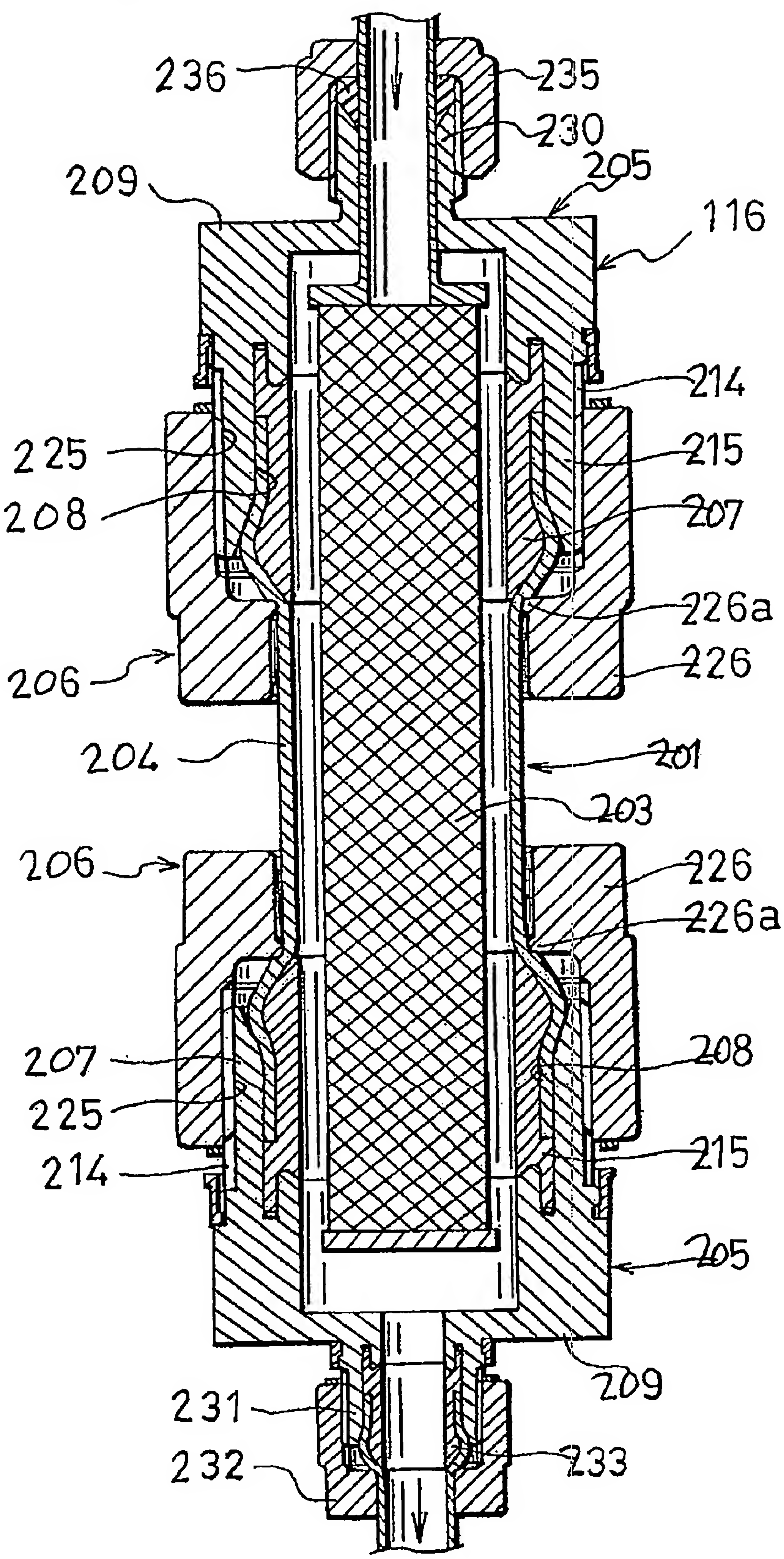
Fig. 8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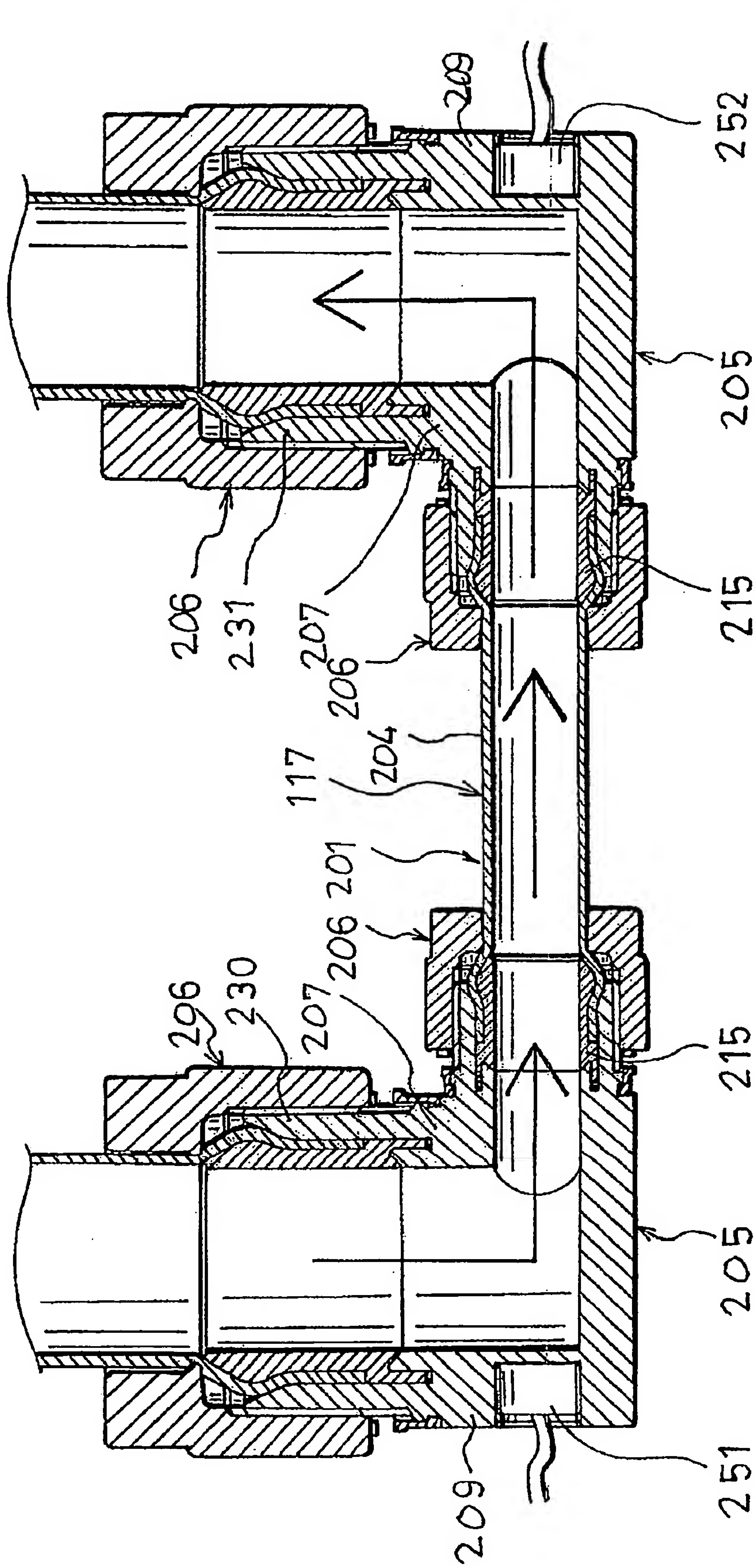
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Fig. 9

Fig. 10

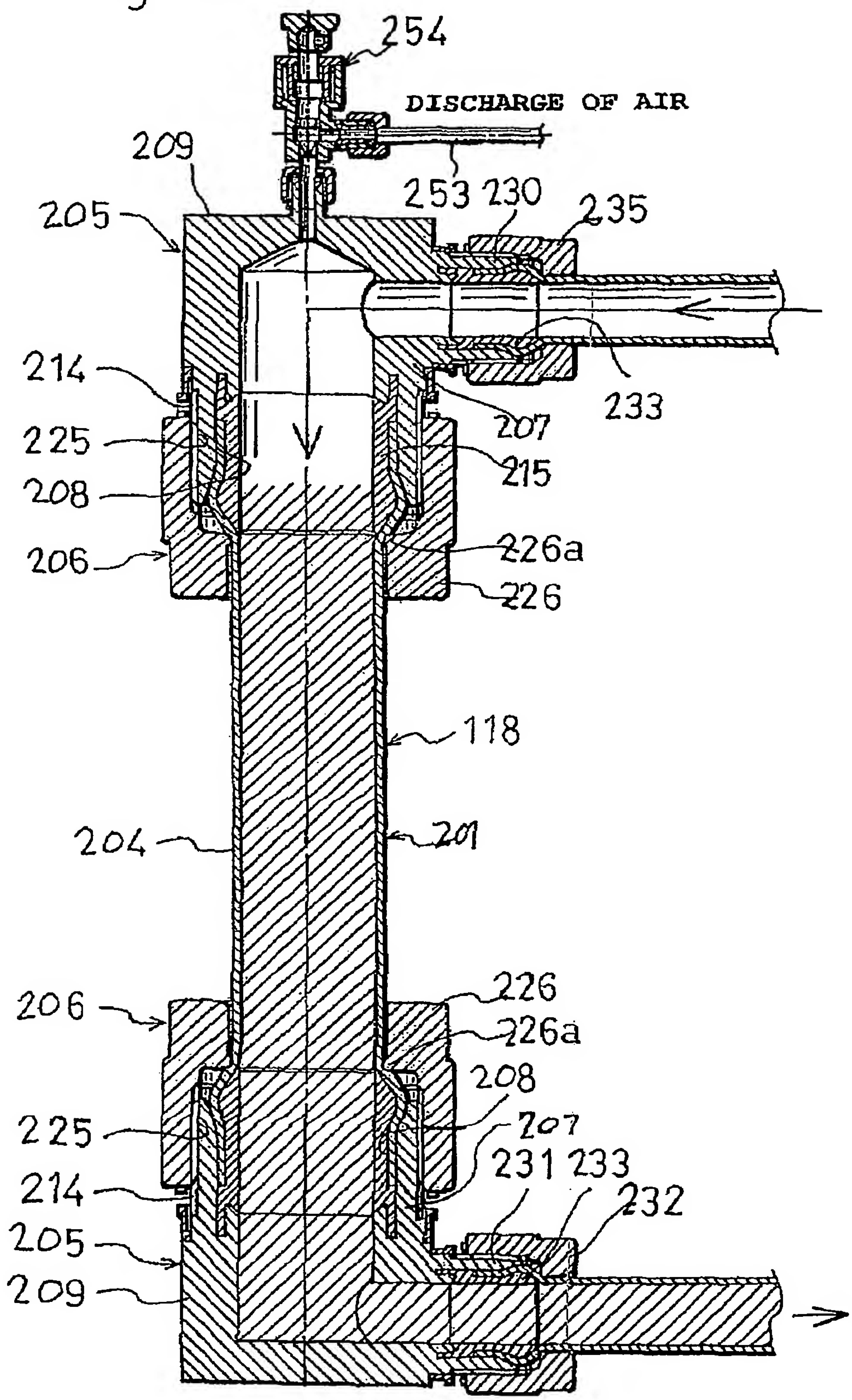
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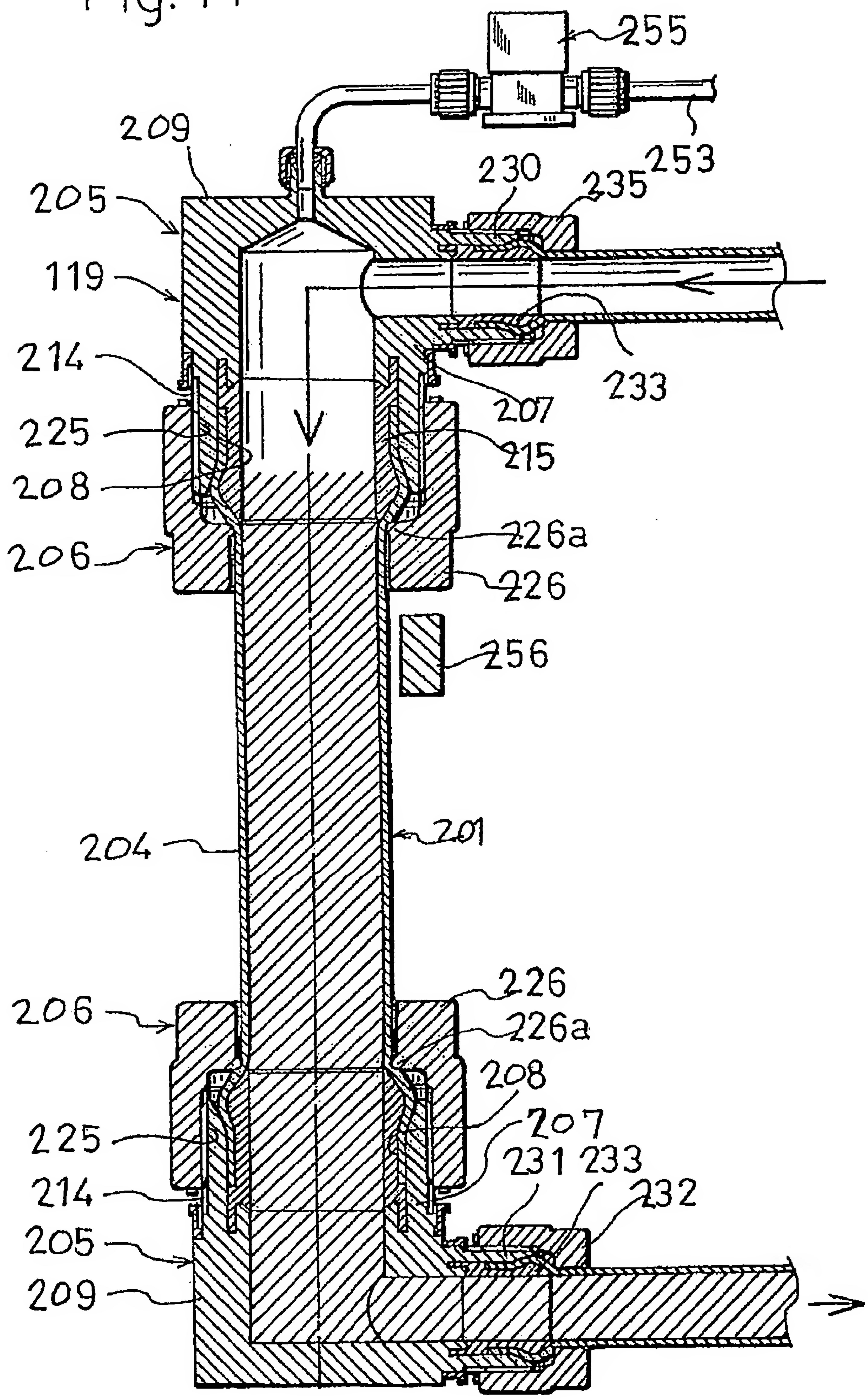
Fig. 11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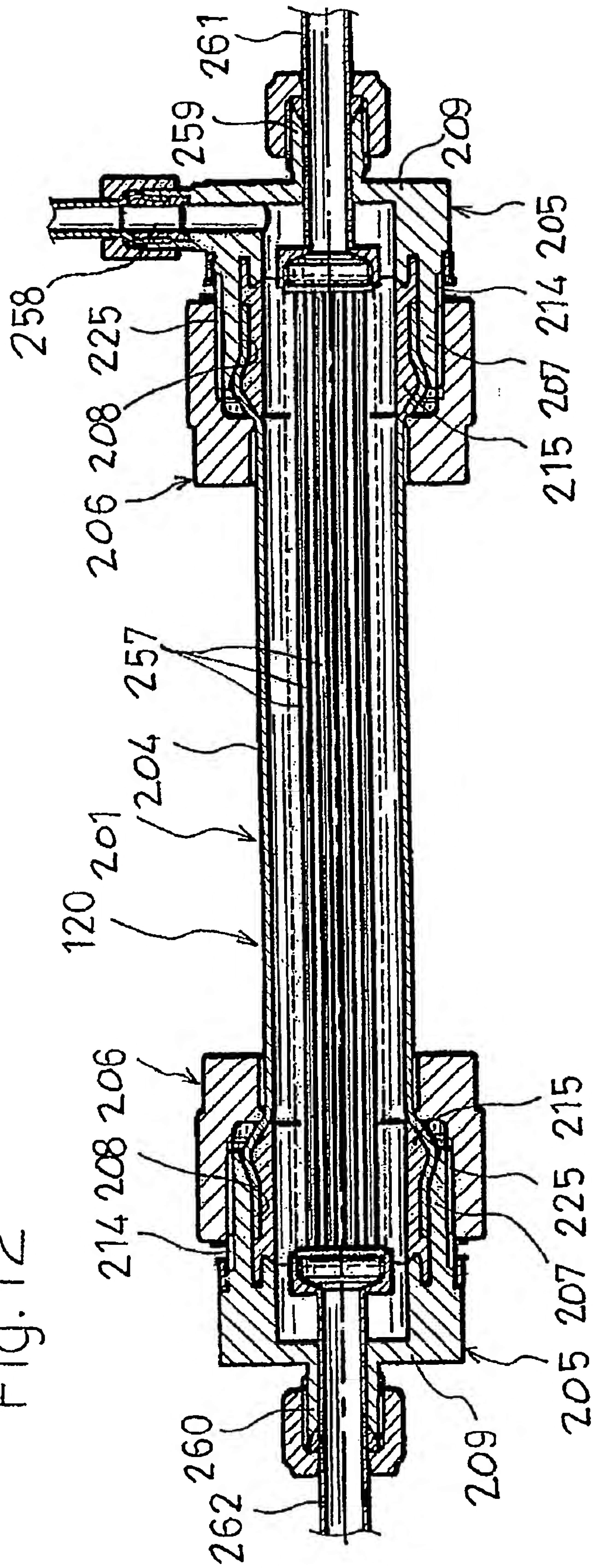
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Fig. 12

Fig. 13

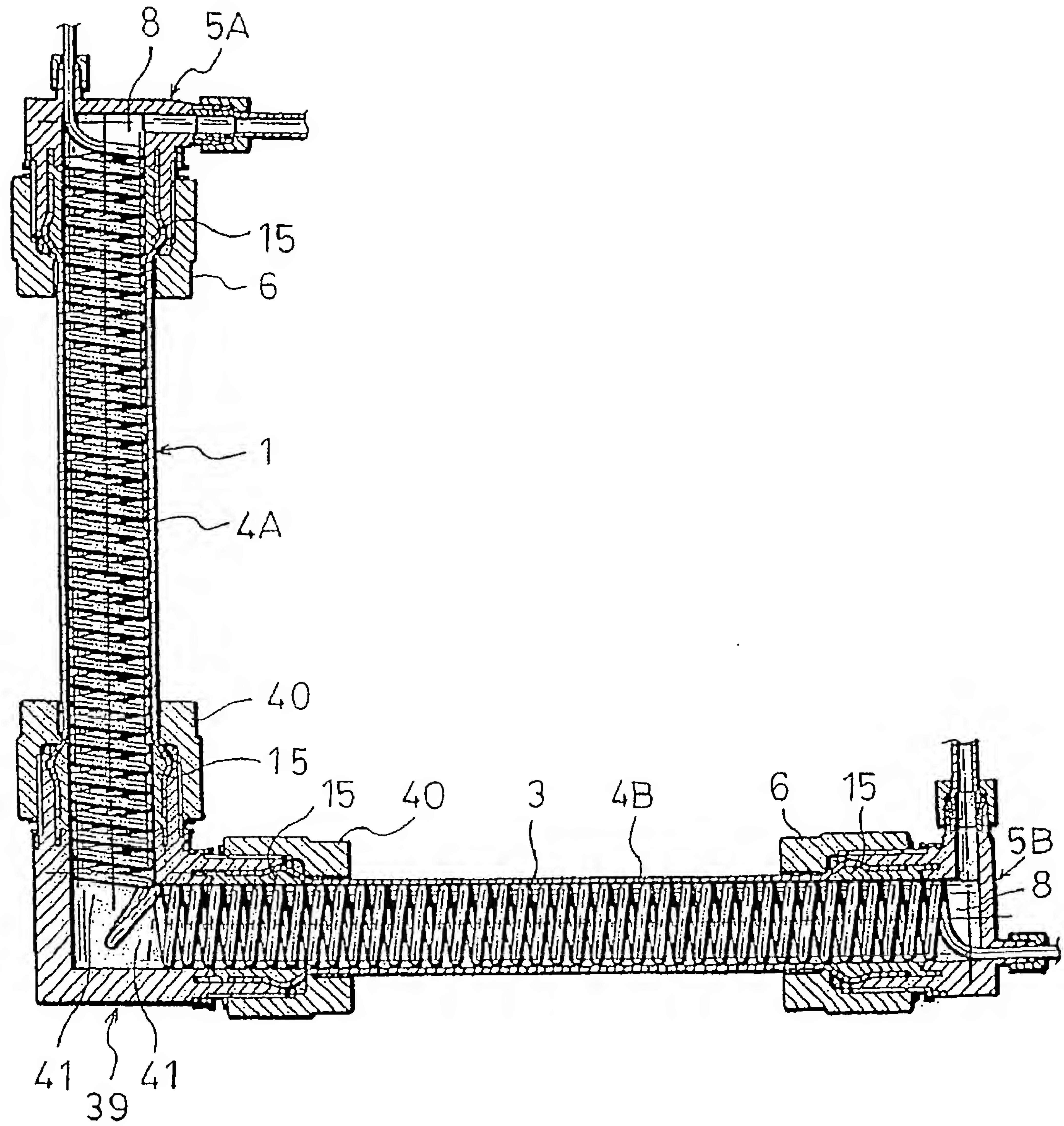

Fig. 14

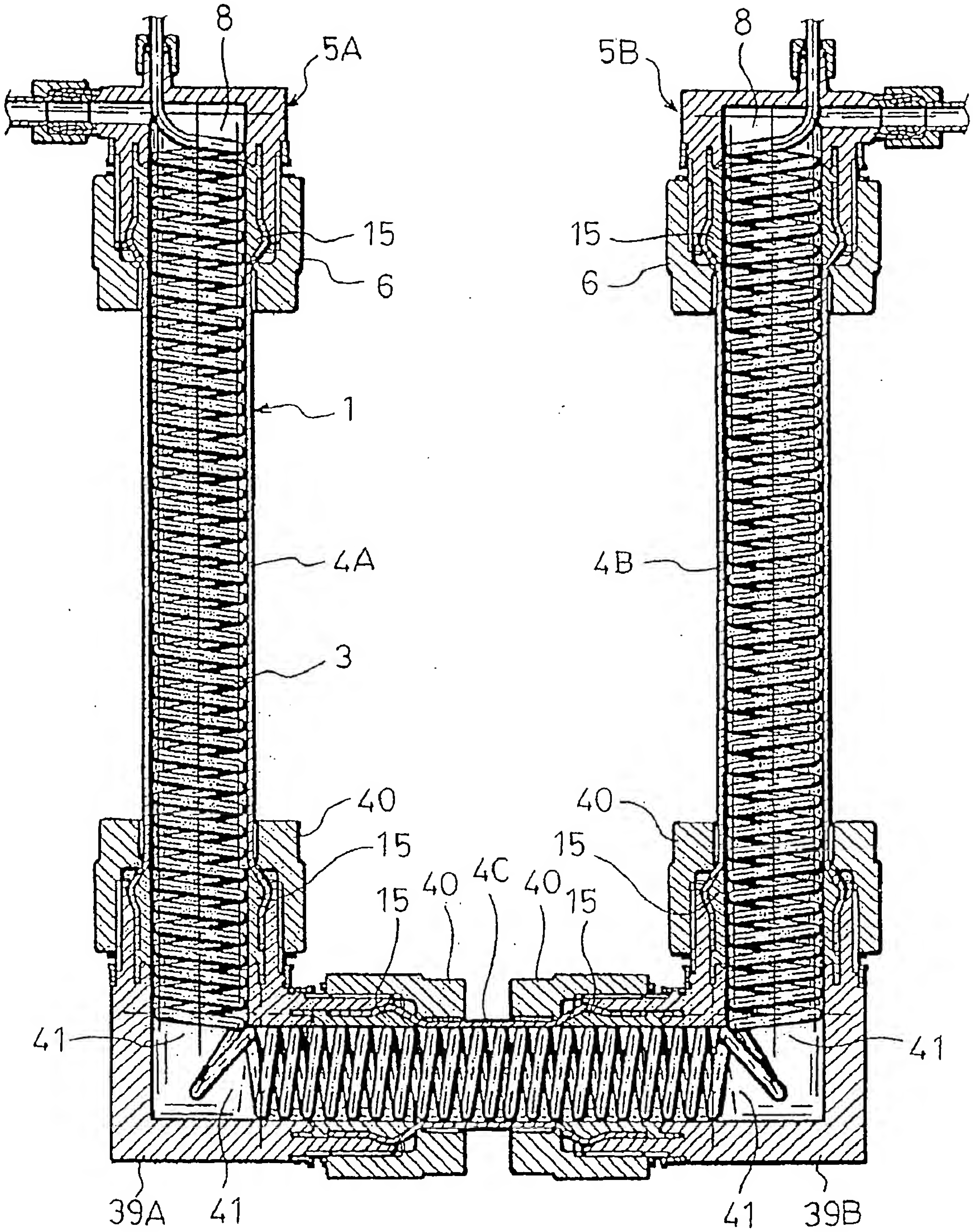
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Fig. 15

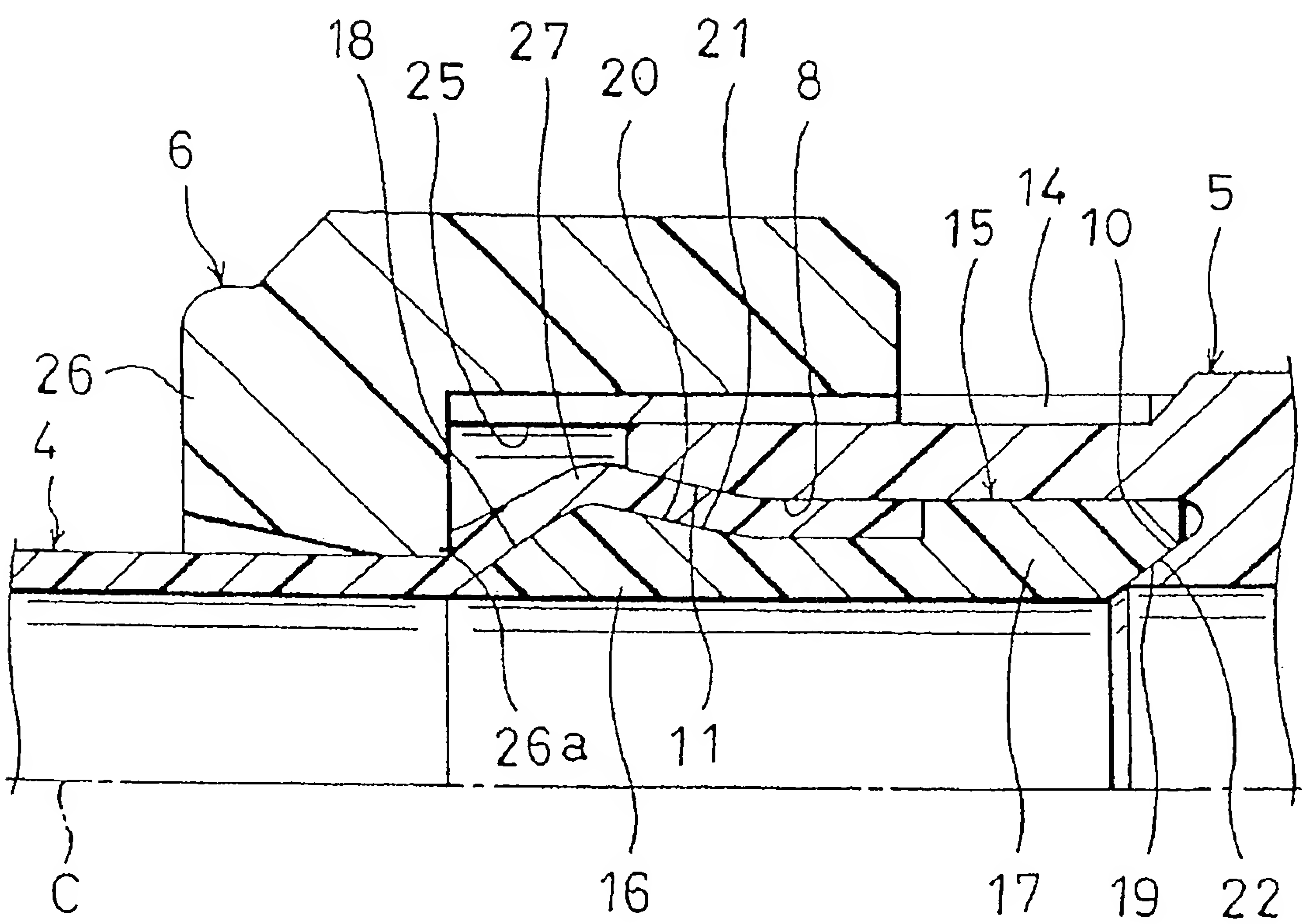


Fig. 16

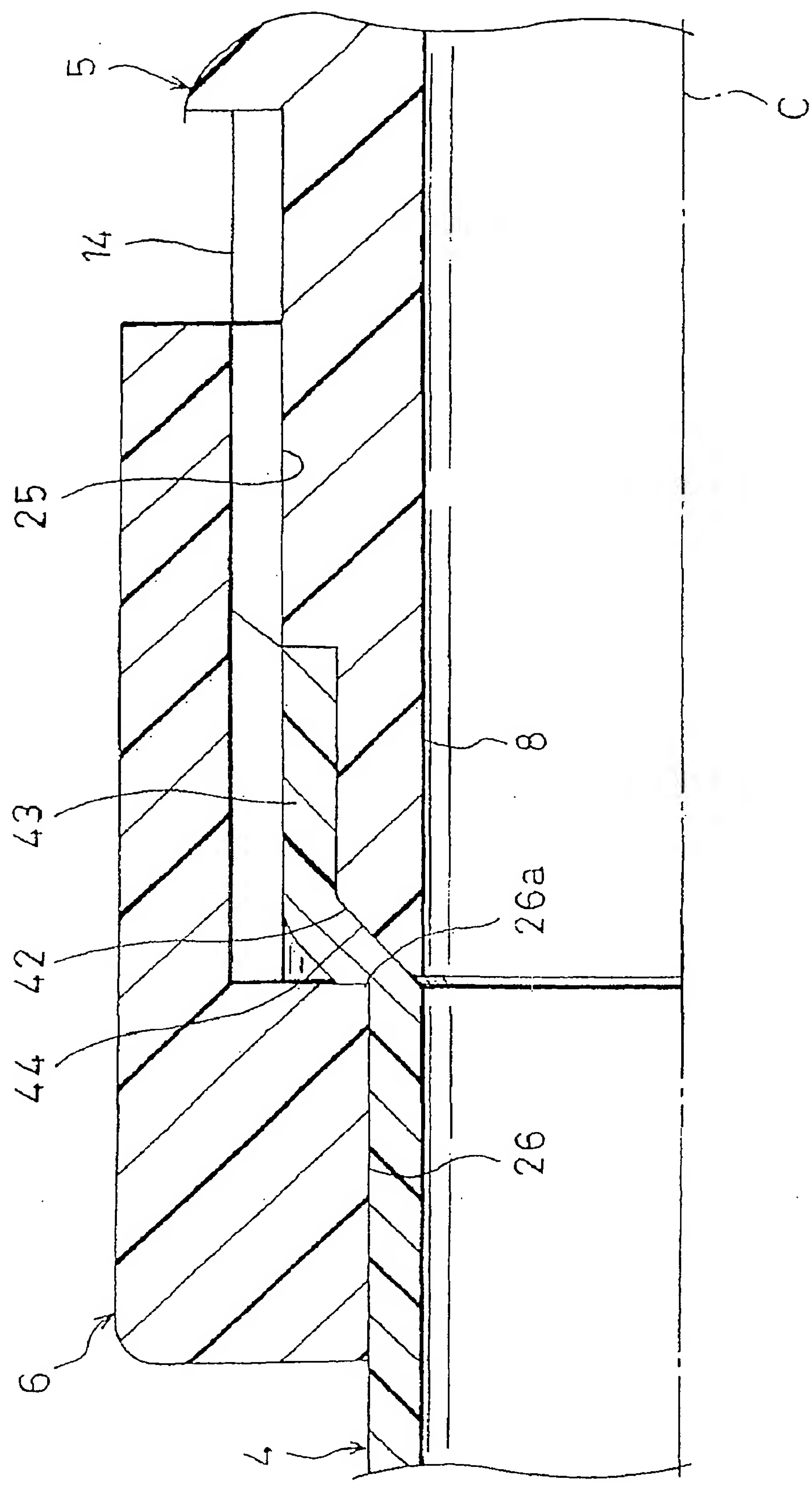


Fig. 17

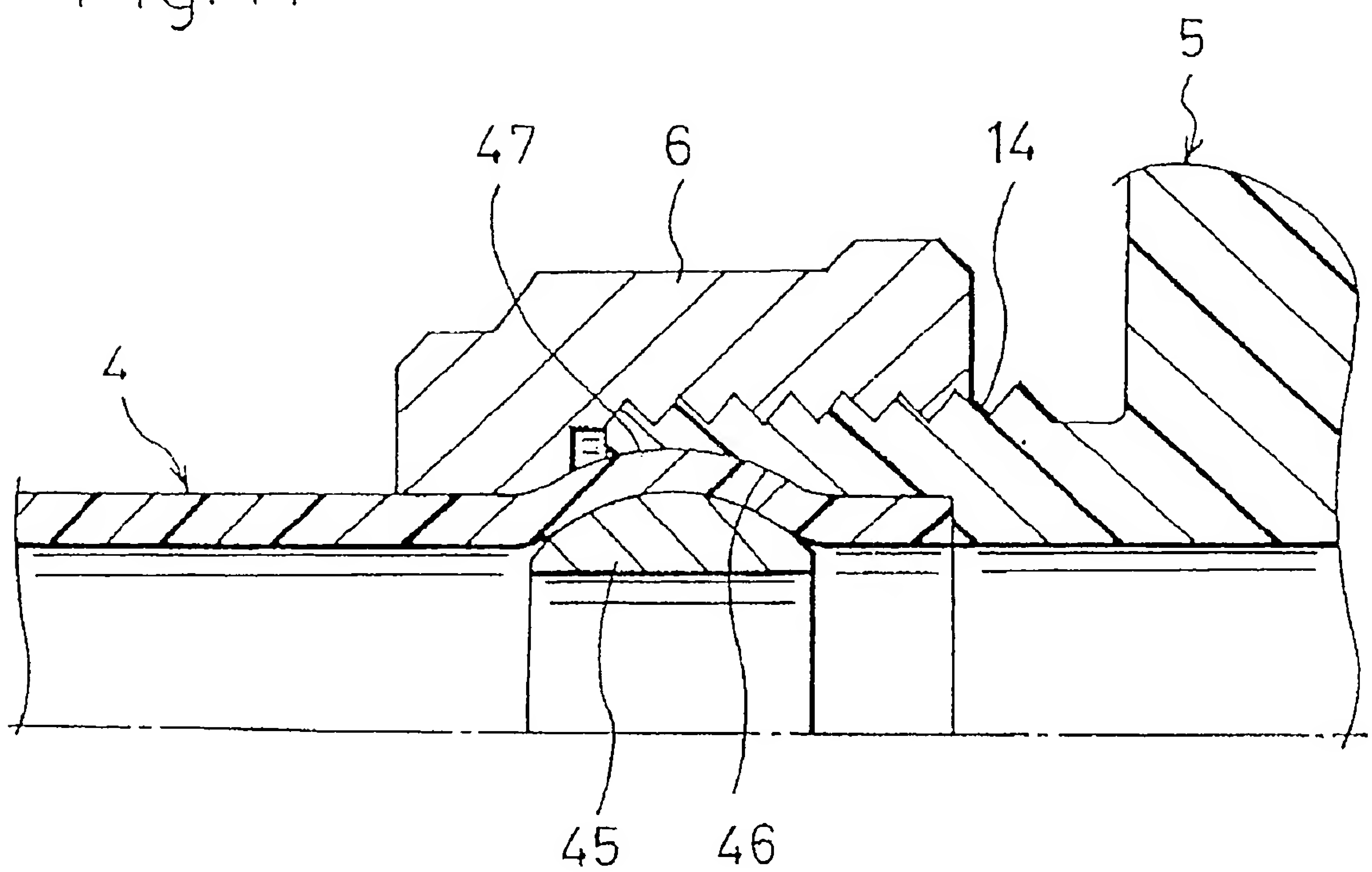
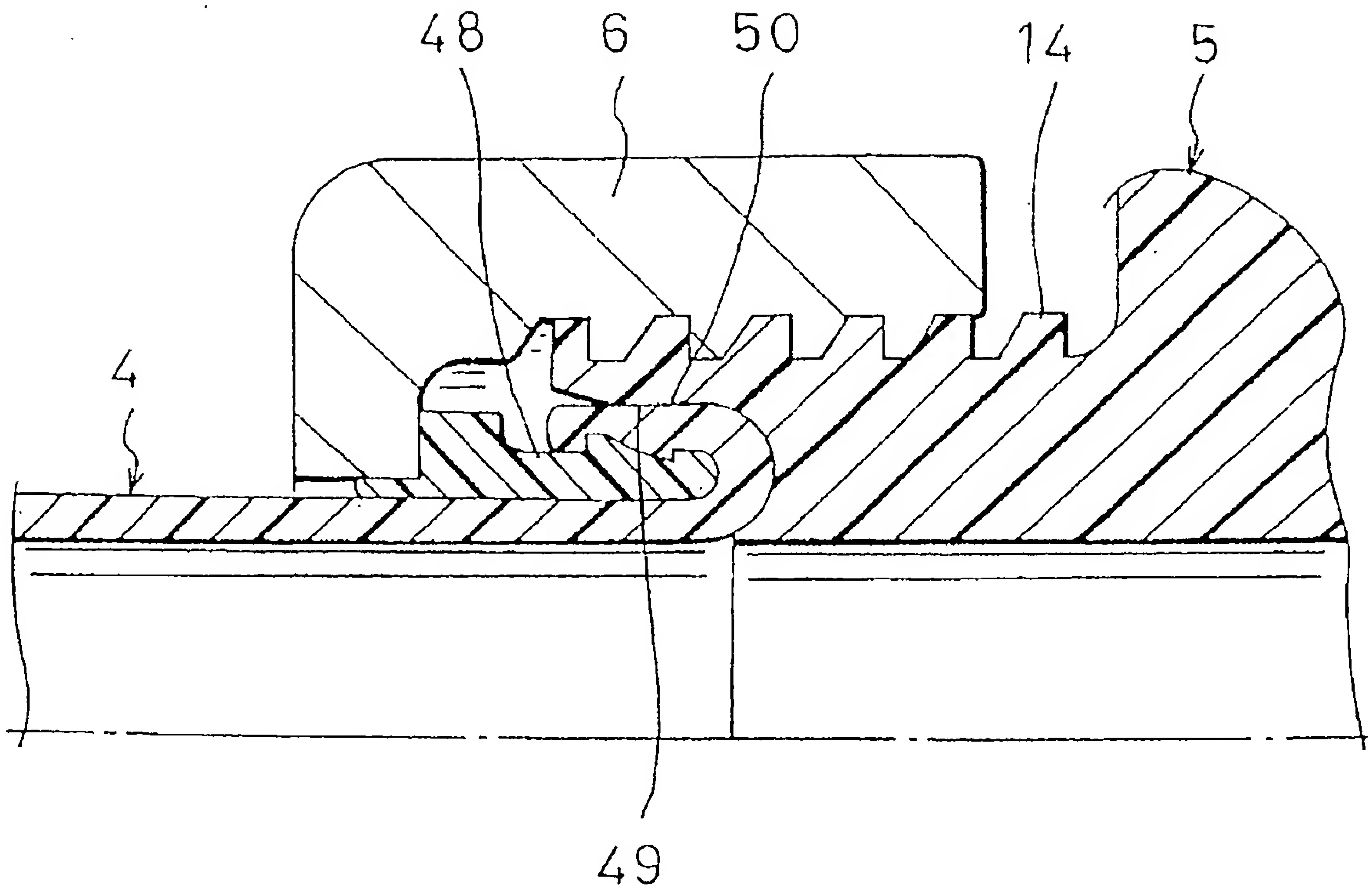


Fig. 18



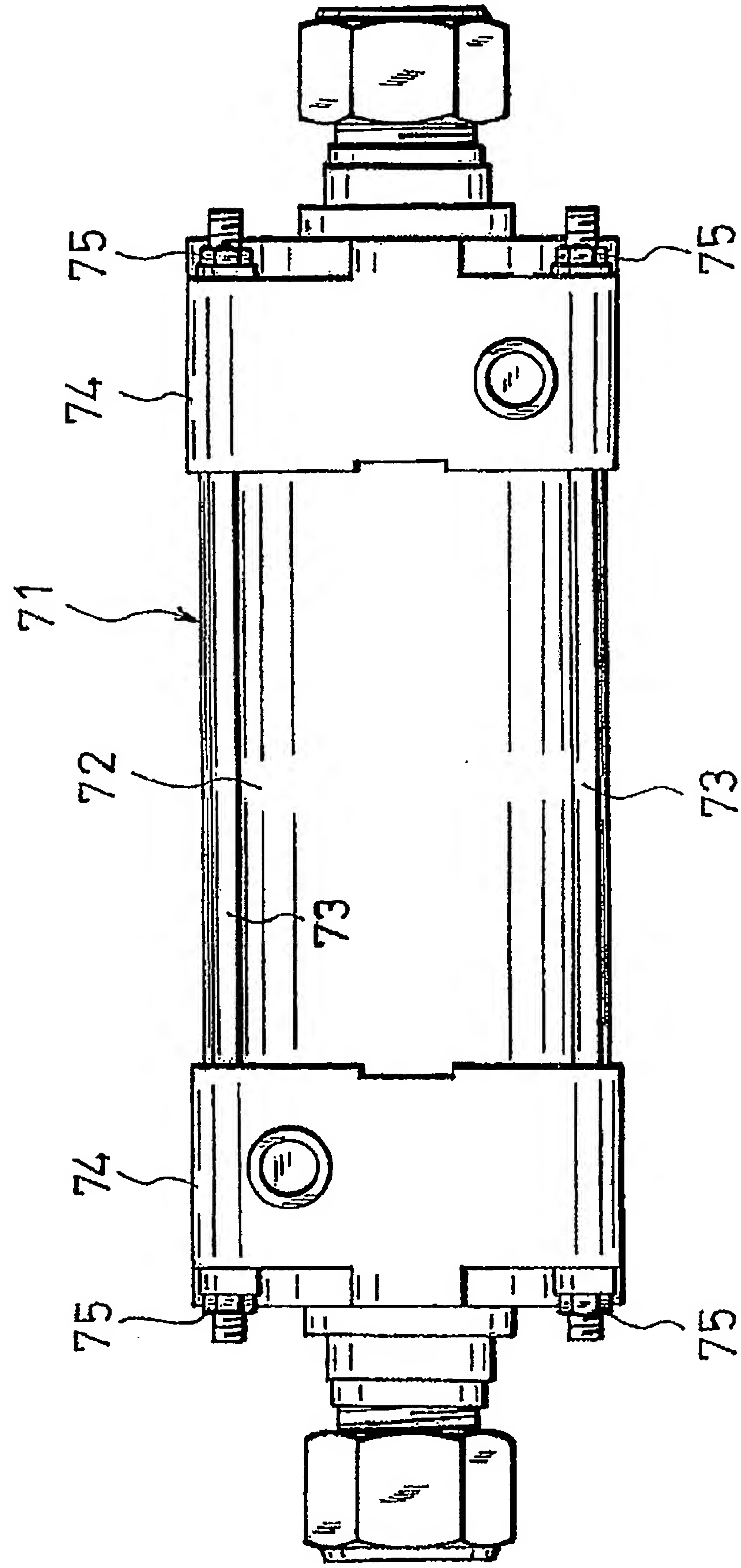


Fig. 19 (Prior Art)

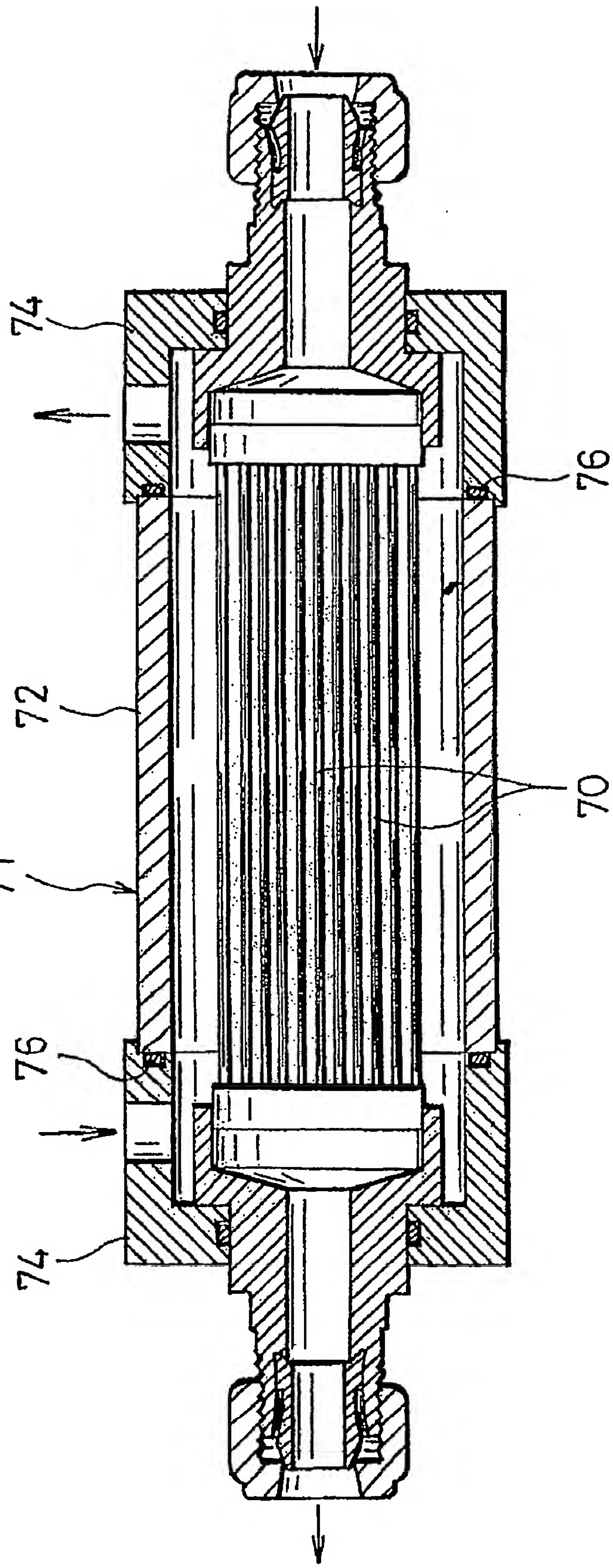


Fig. 20 (Prior Art)

TUBE DEVICE, AND PIPING SYSTEM INCLUDING THE TUBE DEVICE

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a divisional of U.S. patent application Ser. No. 10/844,881, filed May 13, 2004, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to a tube device which is useful in an apparatus for producing semiconductor devices, liquid crystal display devices, or chemicals, a production line for foods, or the like, and also to a piping system including such a tube device.

In a piping system in an apparatus for producing semiconductor devices, liquid crystal display devices, or chemicals, a production line for foods, or the like, higher integrity is required in accordance with the purpose of the piping system. In a piping system for an apparatus for producing semiconductor devices, for example, the number of cleaning steps in various cleaning apparatuses which provide one solution for a semiconductor wet process goes on increasing as the integration of a semiconductor device is advanced. Therefore, cleanness of a cleaning process is requested to attain higher integrity. Consequently, severer requirements are imposed on the technique for cleanly supplying cleaning liquid containing ultra pure water or chemical to a cleaning apparatus. In the current state of the art, chemical is contaminated in processes of mixing, diluting, and transporting in a chemical supplying system. However, the wafer cleanliness must cope with the sub quarter micron age. As a chemical supplying system, known is a system of the mass preparation type. In the system, chemical is pumped from a receiving tank to a diluting and mixing tank to be adjusted to a desired composition or concentration, further pumped from a supplying tank through a long-distance pipe to a storage tank in a wet station, and then supplied via a pump and a filter to a cleaning tank (for example, see Japanese Patent Application Laying-Open Nos. 2000265945 and 1170328).

An example of various tube devices which can be applied to a piping system of such an apparatus for producing semiconductor devices is a heat exchanger shown in FIGS. **19** and **20**. The heat exchanger is configured so that a sufficient sealing property is ensured in a casing **71** through which heat exchange pipes **70** are passed, thereby enabling the casing to withstand an internal pressure of an adequate level. The heat exchanger is structured in the following manner (for example, see Japanese Patent Application Laying-Open No. 10160362). The body of the casing **71** is formed by a cylindrical shell **72**. A plurality of metal fastening members **73** such as tie rods or through bolts are placed parallel to one another on the outer periphery of the shell **72** so as to elongate in the longitudinal direction of the shell. Then both end portions of each of the metal fastening members **73** are passed through lid members **74** which are placed on the end portions of the shell **72**, respectively. Nuts **75** are fastened to external thread portions of the ends of the metal fastening members **73** which project from the lid members **74**, so that the interfaces between the ends of the shell **72** and butting faces of the lid members **74** are closely sealed. As a result, the casing **71** is hermetically sealed. Furthermore, O-rings **76** serving as sealing members are interposed between the ends of the shell **72** and the butting faces of the lid members **74** (see Japanese Patent Application Laying-Open No. 10160362).

In such a chemical supplying system of the mass preparation type, it is recognized as a problem that particles or metal contaminations are produced from various liquid-contacting portions of components of all devices including storage tanks, pipes, joints, pumps, heat exchangers, flow meters, filters, and de-aerating modules.

On the other hand, an enhanced cleaning speed in a substrate cleaning apparatus for cleaning a semiconductor wafer or the like causes a problem in that the whole apparatus is increased in size and complicated. Particularly, a piping system which is configured by various devices is placed in a clean room, and hence requested to be miniaturized and made more compact.

In various tube devices, since metal materials are often used, metal contaminations are produced, and the device shape is fixed. Therefore, the piping system has a low degree of freedom in design, a dead space is easily caused in pipes, and the piping system tends to be increased in size. As a result, in such tube devices including machines such as a cleaning apparatuses, reductions in size and cost are limited. Moreover, there is no device having a shape which can flexibly satisfy a request for modifying an existing piping system. Consequently, modification of a piping system is largely restricted in space.

In the heat exchanger (tube device) in which the interfaces between the end portions of the shell **72** and the lid members **74** are sealed by fastening the nuts **75** to the metal fastening members **73** such as tie rods or through bolts, a large number of components are used for attaining the sealing, and hence the cost and size of the casing structure are increased. In the case where the heat exchanger is installed in a place which is exposed to the sulfuric acid atmosphere or the like, the metal fastening members **73** easily corrode and metal pollution inevitably occurs. Recently, it is therefore highly requested to restrict the use of such metal fastening members in, particularly, the field of semiconductor devices.

In order to avoid loosing of the metal fastening members **73**, it is necessary to periodically refasten the metal fastening members **73**. However, the metal fastening members **73** are generally used in a plural or at least four numbers, and hence the degrees of refastenings of the metal fastening members **73** are easily dispersed. This dispersion may cause the lid members **74** and the shell **72** to be deformed. When the lid members **74** or the shell **72** is deformed, twisting or distortion is produced between the end portions of the shell **72** and the lid members **74**, thereby causing a problem in that local stress concentration occurs to promote development of creep. Moreover, the center axis of a metal tie rod serving as one of the metal fastening members **73** fails to coincide with that of a metal sheath for the tie rod, and the rod and the sheath rub with each other to cause problems in that the sliding resistance is increased, and that abrasion dust containing metal powder is produced. When the shell **72** or the lid members **74** are deformed, such a component must be replaced with a new one. Usually, these components are formed as machined articles, and therefore relatively expensive. Consequently, the heat exchanger has a configuration where reuse in which a device element (for example, the heat exchange pipes **70**) remains to be used also after the casing structure is replaced with a new one is hardly conducted.

In the heat exchanger having the connecting structure in which the O-rings **76** serving as sealing members are interposed between the end portions of the shell **72** and the butting faces of the lid members **74**, the corrosion resistance and the service temperature range are restricted by the use of the O-rings **76**. For example, chemical of a high temperature cannot be passed through a space which is in contact with the

O-rings **76**. Furthermore, dust produced from the O-rings **76** may cause a pollution problem. In the recent field of semiconductor devices, therefore, it is highly requested to restrict the use of such O-rings.

In the case where a heat exchanger of this kind is to be used for chemical or the like, the shell **72**, the lid members **74**, and like components are often made of a fluororesin having excellent corrosion resistance, such as PTFE or PFA. However, a fluororesin has high lubricity, and hence creep due to vibration or heat of a pipe occurs in the connecting portions between the shell **72** and the lid members **74**. As a result, there arises a problem in that the metal fastening members **73** such as tie rods or through bolts are loosened and fluid leakage from the connecting portions in the ends of the shell **72** is caused.

Alternatively, thread sealing or welding may be employed as the casing connecting structure between the shell **72** and the lid members **74**. However, these measures are not highly effective. In a sealing structure which is based simply on threads, a high sealing property cannot be obtained, the pressure resistance is not sufficiently high, and leakage due to creep easily occurs. Usually, welding requires a skilled technique, and cannot be conducted by an easy work. Therefore, the structure due to welding has problems in that the production efficiency is low, that the onsite workability is poor, and that it is difficult to conduct maintenance and inspection on the site.

The invention has been conducted in order to solve the problems. It is an object of the invention to provide a tube device in which metal members such as a metal fastening member are not used and all components can be made of a synthetic resin, whereby the problems of metal elution and production of metal abrasion powder can be solved, and which is preferably used in an apparatus for producing semiconductor devices, and also a piping system including such a tube device.

It is another object of the invention to provide a tube device which can reduce the sizes of various devices, and miniaturize and compactly form a piping system, and which is preferably used in an apparatus for producing semiconductor devices, and also a piping system including such a tube device.

It is a further object of the invention to provide a tube device in which the number of components, and the production cost can be reduced without using a metal fastening member such as a tie rod or a through bolt, and an O-ring, which has a casing structure of high pressure resistance, and a sealing structure of high reliability, and which is preferably used in an apparatus for producing semiconductor devices, and also a piping system including such a tube device.

It is a still further object of the invention to provide a tube device which, even when all components are made of a fluororesin, can ensure a high sealing property, and can be applied to and installed in a chemically resistant atmosphere, and also a piping system including such a tube device.

BRIEF SUMMARY OF THE INVENTION

The tube device of the invention is a tube device including a casing, and a device element which is placed in the casing, wherein the casing comprises: a tube made of a synthetic resin; a pair of lid members which are made of a synthetic resin, and each of which comprises a receiving port for receiving an end portion of the tube, and at least one sealing face disposed in the receiving port; a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of the tube, and which are screwed to end portions of the lid members having the receiving ports, respectively; and a sealing portion which is formed in at least one place for each of the end portions of the tube by closely contacting the end portion of the tube with the sealing face of corresponding one of the lid members, the end portion of the tube and the sealing face of the lid member being closely contacted with each other by causing corresponding one of the union nuts to press the tube from an outside of the tube, the union nut fastening the end portion of the lid member by screw advancement toward the end portion of the lid member, thereby pressing the tube from the outside of the tube. According to the configuration, it is possible to attain the objects.

The piping system of the invention includes a pipe conduit, and the abovementioned tube device which is placed in a middle of the pipe conduit.

In this case, all of the tube, the lid members, and the union nuts may be molded of a fluororesin having excellent heat resistance and corrosion resistance, or an antistatic fluororesin containing an electrically conductive material.

Examples of the device element are as follows. For example, the device element may be configured by: a heat exchange tube which is made of a fluororesin, and which is passed through the casing; and connecting portions to which pipes for introducing and discharging a fluid that is passed between an inner side of the casing and an outer side of the heat exchange tube are connected, respectively. According to the configuration, the tube device can be configured as a heat exchanger. When the device element is a filter member housed in the casing, the tube device can be configured as a filter device. When the device element is configured by an ultrasonic oscillator and an ultrasonic receiver which are used for an ultrasonic flow meter, and which are incorporated in the lid members in the ends of the tube, respectively, the tube device can be configured as an ultrasonic flow meter. When the device element is an air vent valve incorporated in one of the lid members, the tube device can be configured as a de-aerating device. When the device element is configured by gas permeable tubes which are passed through the tube, and a de-aerating port which is disposed in one of the lid members, the tube device can be configured as a de-aerating module. When the device element is configured by gas permeable tubes which are passed through the tube, and a soluble gas supplying port which is disposed in one of the lid members, the tube device can be configured as a gas dissolving device.

The thus configured tube device can be surely hermetically sealed by the sealing portion in which the end portion of the tube and the sealing face of the lid member are closely contacted with each other by a simple operation of fastening the union nut to an end portion of the lid member. Therefore, it is possible to obtain a tube device in which, unlike the conventional art, the number of components, and the production cost can be reduced without using a metal fastening member such as a tie rod or a through bolt, and an O-ring, and which has a casing structure of high pressure resistance, and a sealing structure of high reliability, and also a piping system including such a tube device.

In the tube device, a pressure tight sealing structure in which, unlike the conventional casing connecting structure, tie rods or through bolts are not used, and a slim casing structure can be realized, and the sealing property can be uniformly ensured by refastening a single union nut. In the tube device, namely, a sealing structure which is higher in reliability than the case where tie rods or through bolts are used can be obtained simply by sealing each of the connecting portions between the end portions of the tube and the lid members with the single union nut. Moreover, the tube device having the slim casing enables a piping system to be minia-

turized and compacted. In the tube device, the sealing property can be ensured at any time by refastening the union nuts, and hence the reliability is maintained to be high for a longer term as compared with the case where thread sealing or O-ring sealing is used. In the tube device, it is necessary only to conduct only simple means that the single union nut is refastened. Unlike the connecting structure due to welding, therefore, the work on the site is facilitated, and maintenance and inspection on the site can be easily conducted.

Since no metal member such as a metal fastening member is used, it is possible to solve the problems of metal elution and production of metal abrasion powder.

When the union nut is fastened, the whole outer circumference of the end portion of the tube can be uniformly pressed, and hence the tube and the lid member are prevented from being accidentally deformed. Therefore, it is possible to solve the problems of creep and replacement of these members.

When the union nut is loosened, the lid member can be easily detached from the end portion of the tube. Therefore, stagnate fluid which stagnates in the tube can be easily removed away.

In the tube device to be placed in a pipe conduit of the piping system, even when an internal pressure arises in the tube, the air tightness can be maintained simply by the fastening of the union nut, and fluid leakage can be prevented from occurring. Unlike the conventional art, therefore, the use of an O-ring can be eliminated, and all the components can be molded of a fluororesin. As a result, the tube device can sufficiently cope with high temperature and strong corrosive chemical, and can be applied to and installed in a chemically resistant atmosphere.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

The foregoing summary, as well as the following detailed description of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown.

In the drawings:

FIG. **1** is a diagram showing the whole configuration of an apparatus for cleaning a semiconductor wafer (substrate) including a chemical supply piping system which is an example of the piping system of the invention;

FIG. **2** is a section view of a heat exchanger which is an example of the tube device of the embodiment of the invention shown in FIG. **1**;

FIG. **2***a* is a fragmentary view of an inlet port of the heat exchanger shown in FIG. **2**;

FIG. **2***b* is a fragmentary view of an outlet port of the heat exchanger shown in FIG. **2**;

FIG. **3** is an enlarged section view of a structure for connecting an end portion of a tube and a lid member of the heat exchanger of FIG. **2**;

FIG. **4** is a section view showing another example of the heat exchange tube of the heat exchanger of FIG. **2** in a manner corresponding to FIG. **2**;

FIG. **5** is a section view showing a further example of the heat exchange tube of the heat exchanger of FIG. **2** in a manner corresponding to FIG. **2**;

FIG. **6** is a section view showing a still further example of the heat exchange tube of the heat exchanger of FIG. **2** in a manner corresponding to FIG. **2**;

FIG. **7** is a section view of a filter device which is another example of the tube device of the embodiment of the invention;

FIG. **8** is a section view showing another example of the filter device of the embodiment of the invention;

FIG. **9** is a section view of an ultrasonic flow meter which is a further example of the tube device of the embodiment of the invention;

FIG. **10** is a section view of a manual de-aerating device which is a still further example of the tube device of the embodiment of the invention;

FIG. **11** is a section view of an automatic de-aerating device which is a still further example of the tube device of the embodiment of the invention;

FIG. **12** is a section view of a de-aerating module which is a still further example of the tube device of the embodiment of the invention;

FIG. **13** is a section view showing another example of a casing of the tube device of the embodiment of the invention;

FIG. **14** is a section view showing a further example of the casing of the tube device of the embodiment of the invention;

FIG. **15** is a section view showing another example of a sealing portion of the tube device of the embodiment of the invention;

FIG. **16** is a section view showing a further example of the sealing portion of the tube device of the embodiment of the invention;

FIG. **17** is a section view showing a still further example of the sealing portion of the tube device of the embodiment of the invention;

FIG. **18** is a section view showing a still further example of the sealing portion of the tube device of the embodiment of the invention;

FIG. **19** is a front view of a tube device (heat exchanger) of a conventional art example; and

FIG. **20** is a section view of the heat exchanger of FIG. **19**.

DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments of the invention will be described with reference to the accompanying drawings.

FIG. **1** is a diagram showing the whole configuration of an apparatus for cleaning a semiconductor wafer (substrate) including a chemical supply piping system which is an example of the piping system of the invention. In the figure, A denotes a cleaning chamber in which a wafer (substrate) W is disposed to be cleaned, and B denotes a chemical supply piping system which produces cleaning liquid of a desired concentration and supplies the liquid to the cleaning chamber A. The chemical supply piping system B comprises: a chemical storage tank **100** which stores chemical in an undiluted state; a chemical supplying apparatus **101** which is connected to the chemical storage tank **100**, and which supplies the chemical; a supply pipe **102** which is connected to the chemical supplying apparatus **101**, and which functions as a path of ultra pure water mixed with the chemical; a pair of ejection nozzles **103**, **104** which are disposed in a downstream portion of the supply pipe **102** so as to be opposed to surfaces of the wafer W disposed in the cleaning chamber A; and a control system **105** which adjusts various states such as the concentration and flow amount of the cleaning liquid supplied from the ejection nozzles **103**, **104**.

The chemical supplying apparatus **101** comprises: a chemical supplying pump **106**; a connecting pipe **107** which connects the supply pipe **102** to the chemical supplying pump **106** to form a flow path; and a capillary **108** which directly connects the interior of the connecting pipe **107** to that of the

supply pipe **102**. When the chemical supplying pump **106** is driven, the chemical is ejected from the capillary **108** into the ultra pure water in the supply pipe **102**.

In the supply pipe **102**, disposed are: flow amount adjusting means **109** for adjusting the flow amount of the ultra pure water passed through the supply pipe **102**; concentration adjusting means **110** for adjusting the concentration of the cleaning liquid passed through the supply pipe **102**; and mixing means **111**, placed in a portion where the supply pipe **102** and the capillary **108** are connected to each other, for producing a rotating flow in the cleaning liquid to stir it, thereby uniformalizing the cleaning liquid.

The control system **105** comprises: chemical supply controlling means **112** for adjusting the amount of the chemical to be supplied to the ultra pure water by the chemical supplying pump **106**, and for driving the flow amount adjusting means **109**; and concentration controlling means **113** for driving the concentration adjusting means **110**. The chemical supply controlling means **112** and the concentration controlling means **113** are connected to each other. A result of the concentration control by the concentration controlling means **113** is fed back to the chemical supply controlling means **112** to control the chemical supplying pump **106**, whereby the supply amount of the chemical is adjusted.

The invention is characterized in that a tube device selected from various kinds of tube devices is disposed in an adequate place of the pipes in the chemical supply piping system B, and the tube device is configured in the following manner.

FIG. 1 shows an embodiment in which a heat exchanger **114** that is a tube device is disposed in the middle of the supply pipe **102** that is a pipe of the chemical supply piping system B. As shown in FIG. 2, the heat exchanger **114** conducts heat exchange between a fluid passed through a heat exchange tube **3** which is passed through the interior (heat exchange chamber) **2** of a casing **1**, and that is passed between the interior of the casing **1** and the outside of the heat exchange tube **3**.

As shown in FIGS. 2 and 3, the casing **1** comprises: a tube **4** surrounding the outer periphery of the heat exchange tube **3**; a pair of lid members **5** which hermetically close one and other end portions of the tube **4**, respectively; and union nuts **6** which fasten the lid members **5** to the end portions of the tube **4**, respectively.

The tube **4** is molded of a synthetic resin, for example, a fluororesin having excellent heat resistance and corrosion resistance, such as PFA or PTFE, or an antistatic fluororesin containing an electrically conductive material, into a cylindrical shape. The lid members **5** which are similarly made of a synthetic resin such as a fluororesin are inserted into the end portions of the tube **4**, and connected thereto by fastening the union nuts **6** made of a synthetic resin such as a fluororesin, respectively.

Each of the lid members **5** is formed into a shape having: a body wall portion **7**; a receiving portion **8** which is opened in one end of the body wall portion **7**; and a bottom wall portion **9** which closes the other end of the body wall portion **7**. As shown in FIG. 3, first to third sealing faces **10** to **12** are disposed inside the receiving portion **8** of the lid member **5**. The first sealing face **10** is configured by a tapered face which is formed inner than the entrance of the receiving portion **8** of the lid member **5**, and in which the diameter is gradually increased so as to intersect with the axis C of the lid member **5**, or toward the outer side in the direction of the axis C. The second sealing face **11** is configured by a tapered face which is formed in the entrance of the receiving portion **8**, and in which the diameter is gradually increased so as to intersect with the axis C, or toward the outer side in the direction of the axis C. The third sealing face **12** is configured by an annular groove **13** which is formed in an inner portion of the receiving portion **8** of the lid member **5** and in the radially outer side with respect to the first sealing face **10**, and which elongates parallel to the axis C. An external thread portion **14** is formed on the outer periphery of the receiving portion **8** of the lid member **5**.

On the other hand, inner rings **15** made of a synthetic resin such as a fluororesin are pressingly inserted into the one and other end portions of the tube **4**, respectively. As shown in FIG. 3, the inner rings **15** are formed into a sleeve-like shape having: a press-insertion portion **16** which has an abacus beadlike section shape, and which is to be pressingly inserted into the corresponding end portion of the tube **4** to increase the diameter of the end portion, thereby expanding the end portion so as to have a mountain-like section shape; and a projection portion **17** which is continuous to the press insertion portion **16**, and which is to project from the end portion of the tube **4**. In the press insertion portion **16** having an abacus beadlike section shape, an outward tapered face **18** is formed on one inclined face of the portion, and an inward tapered face **20** which cooperates with the second sealing face **11** to pressingly hold the end portion of the tube **4** in an inclined state to form a second sealing portion **21** is formed on the other inclined face. A projection end face **22** formed by a tapered face which butts against the first sealing face **10** to be in close contact therewith to form a first sealing portion **19**, and a cylindrical portion **24** which is to be fitted into the annular groove **13** to form a third sealing portion **23** are formed in the tip end of the projection portion **17**. The inner diameter of the inner ring **15** is set to be equal to or substantially equal to that of the tube **4**, thereby allowing the fluid flowing through the inner ring **15** and the tube **4** to smoothly flow without stagnating in the interface between the inner ring **15** and the tube **4**.

As shown in FIG. 3, an internal thread portion **25** which is to be screwed with the external thread portion **14** of the lid member **5** is formed in the internal periphery of the union nut **6**, an annular flange **26** is inwardly projected from one end portion of the union nut **6**, and a pressing edge **26***a* having an acute or right angle is disposed in an axially inner end of the inner peripheral face of the annular flange **26**.

The end portion of the tube **4** into which the inner ring **15** is pressingly inserted is inserted into the receiving portion **8** of the lid member **5**, and the internal thread portion **25** of the union nut **6** which is previously loosely fitted to the outer periphery of the end portion of the tube **4** is screwed with the external thread portion **14** of the lid member **5** to be fastened up. In accordance with this fastening, the pressing edge **26***a* of the union nut **6** butts against an expansion basal portion of a long diameter portion **27** of the tube **4** to axially press the inner ring **15**. As a result, as shown in FIG. 3, the projection end face **22** of the inner ring **15** is pressed against the first sealing face **10** of the lid member **5** to form the first sealing portion **19**, and the end portion of the tube **4** is pressingly held in an inclined state between the inward tapered face **20** of the inner ring **15** and the second sealing face **11** of the lid member **5**, thereby forming the second sealing portion **21**. Furthermore, the cylindrical portion **24** of the inner ring **15** is pressingly inserted into the annular groove **13** to form the third sealing portion **23**. The first to third sealing portions **19**, **21**, **23** exert a sealing function of high reliability.

As shown in FIG. 2, the lid member **5** in the one end portion of the tube **4** comprises a connecting portion **29***a* to which a heat exchange fluid inlet pipe **28***a* that is another pipe is to be connected, and the lid member **5** in the other end portion comprises a connecting portion **29***b* to which an outlet pipe

28*b* that is another pipe is to be connected. The connecting portions 29*a*, 29*b* which are to be connected to other pipes are configured in the following manner. An inlet port **30** for a heat exchange fluid such as temperature controlled water is formed in the body wall portion **7** of the one lid member **5**, and an outlet port **31** is formed in the body wall portion **7** of the one lid member **5**. End portions of the heat exchange fluid inlet and outlet pipes **28***a*, **28***b* are connected respectively to the inlet and outlet ports **30**, **31** via a union nut **32** and an inner ring **33** which are made of a synthetic resin such as a fluororesin, so that the heat exchange fluid flows through the inlet port **30**, the heat exchange chamber **2** of the tube **4**, and the outlet port **31** in this sequence.

The internal structures of the inlet port **30** and the outlet port **31** are configured in the same manner as the internal structures (except the diameters) of the receiving portions **8** of the lid members **5**. The inner rings **33** which are identical in section shape as the inner rings **15** for the end portions of the tube **4** are pressingly inserted into end portions of the heat exchange fluid inlet and outlet pipes **28***a*, **28***b*, respectively. In the end portions of the inlet and outlet pipes **28***a*, **28***b*, the structures for connecting with the inlet port **30** and the outlet port **31** are identical with those of the end portions of the tube **4** for connecting with the receiving portions **8** of the lid members **5**, and hence their detailed description is omitted. Alternatively, other means such as that for directly welding or screwing the end portions of the heat exchange fluid inlet and outlet pipes **28***a*, **28***b* with the inlet port **30** and the outlet port **31** may be employed as the structures for connecting the end portions of the heat exchange fluid inlet and outlet pipes **28***a*, **28***b* to the inlet port **30** and the outlet port **31**. Namely, the connecting portions **29***a*, **29***b* may be realized by connecting means such as welding or screw connection.

Referring to FIGS. **2**, **2***a* and **2***b*, the heat exchange tube **3** formed by a coil tube which is made of a synthetic resin such as a fluororesin, and through which chemical is to flow is passed through the interior of the tube **4**. The end portions of the heat exchange tube **3** are led out from outlet ports **34** which are opened in the bottom wall portions **9** of the lid members **5**, respectively, and then connected to a middle portion of the supply pipe **102** of the pipe conduit of the chemical supply piping system B, as shown in FIG. **1**. Union nuts **35** made of a synthetic resin such as a fluororesin are fitted onto the led-out end portions of the heat exchange tube **3**, respectively. The union nuts **35** are fastened to the outlet ports **34** via ferrules **36** made of a synthetic resin such as a fluororesin, whereby the gaps between the outlet ports **34** and the end portion of the heat exchange tube **3** are hermetically sealed.

In the thus configured heat exchanger, heat exchange is conducted between a fluid such as chemical passed through the interior of the heat exchange tube **3**, and the heat exchange fluid such as temperature controlled water passed through the outer side the heat exchange tube **3** in the cylindrical casing body of the tube **4**. In place of the configuration in which a fluid such as chemical is passed through the inner side of the heat exchange tube **3** and the heat exchange fluid such as temperature controlled water is passed through the outer side of the heat exchange tube **3**, an opposite configuration in which the heat exchange fluid such as temperature controlled water is passed through the inner side of the heat exchange tube **3**, and a fluid such as chemical is passed through the outer side of the heat exchange tube **3** may be employed.

As shown in FIG. **4**, alternatively, the end portions of the heat exchange tube **3** may be led out from outlet ports **34** which are opened in the body wall portions **7** of the lid members **5**, and the inlet and outlet ports **30**, **31** for a fluid such as chemical may be disposed in the bottom wall portions **9** of the lid members **5**, respectively.

As shown in FIG. **5**, alternatively, the heat exchange tube **3** through which a fluid such as chemical or the heat exchange fluid such as temperature controlled water is passed may be formed by a single straight tube made of a fluororesin. In the alternative also, in the same manner as the case shown in FIG. **3** in which the heat exchange tube is formed by a coil tube, the end portions of the heat exchange tube **3** are led out from outlet ports **34** which are opened in the bottom wall portions **9** of the lid members **5**. Union nuts **37** made of a synthetic resin such as a fluororesin are fitted onto the led-out end portions of the heat exchange tube **3**, respectively. The union nuts **37** are fastened to the outlet ports **34** via ferrules **38** made of a synthetic resin such as a fluororesin, whereby the gaps between the outlet ports **34** and the end portions of the heat exchange tube **3** are hermetically sealed.

As shown in FIG. **6**, alternatively, the heat exchange tube **3** through which a fluid such as chemical or the heat exchange fluid such as temperature controlled water is passed may be formed by plural straight tubes made of a fluororesin which are similar to those in the conventional heat exchanger shown in FIG. **20**.

Other Embodiments of the Tube Device

In place of the heat exchanger **114**, other devices such as filter devices shown in FIGS. **7** and **8**, an ultrasonic flow meter shown in FIG. **9**, a manual de-aerating device shown in FIG. **10**, an automatic de-aerating device shown in FIG. **11**, and a de-aerating module shown in FIG. **12** may be employed as the tube device. Each of the devices is disposed in an adequate place of the pipe conduit in the chemical supply piping system B in accordance with its unique function.

Referring to FIG. **7**, in the filter device **115**, a filter member **203** serving as a device element is housed in the casing **201**. For example, the filter member **203** is configured in the following manner. Functional powder of ceramics, activated charcoal, titanium oxide, or a like material is carried in a carrier such as synthetic fibers. For example, pure water which flows into the casing from the inlet port **230** disposed in the lid member **205** is passed through the filter member **203** to be converted to ultra pure water. Alternatively, an ion-exchange resin such as silica gel may be carried in a carrier, and pure water or chemical which flows into the casing from the inlet port **230** is passed through the filter member **203** to remove away metal ions contained in the pure water or chemical.

The casing **201** of the filter device **115** comprises: the tube **204**; the lid members **205** which hermetically close the both end portions of the tube **204**, respectively; and the union nuts **206** which fasten the lid members **205** to the end portions of the tube **204**, respectively. The inlet port **230** and the outlet port **231** disposed in the lid members **205** are connected to adequate places of the pipe conduit of the chemical supply piping system B, as shown in FIG. **1**. The tube **204**, the lid members **205**, and the union nuts **235** are configured in the same manner as those of the heat exchanger **114** shown in FIG. **2**. Therefore, the identical members and elements are denoted by the same reference numerals, and their description is omitted.

FIG. **8** shows another example of the filter device. In the filter device **116**, the filter member **203** formed by a hollow fiber membrane serving as a device element is housed in the casing **201**, and, for example, pure water is passed through the filter member **203** to be converted to ultra pure water. Other configuration is identical with that of the filter device **115**

shown in FIG. 7. Therefore, the identical members and elements are denoted by the same reference numerals, and their description is omitted.

Referring to FIG. 9, in the ultrasonic flow meter **117**, in the same manner as the case of the heat exchanger **114**, the casing **201** comprises: the tube **204**; the lid members **205** which hermetically close the both end portions of the tube **204**, respectively; and the union nuts **206** which fasten the lid members **205** to the end portions of the tube **204**, respectively. As a device element, an ultrasonic oscillator **251** for the ultrasonic flow meter is incorporated in the bottom wall portion **209** of one of the lid members **205** for the ends of the tube **204** of the casing **201**, and an ultrasonic receiver **252** is incorporated in the bottom wall portion **209** of the other lid member **205**.

The ultrasonic flow meter **117** can measure the flow amount on the basis of a phenomenon that an ultrasonic wave is Doppler-shifted by the flow of pure water, ultra pure water, chemical, or the like which enters into the casing from the inlet port **230** disposed in the body wall portion **207** of the one lid member **205**, and flows through the tube **204** toward the outlet port **231** disposed in the other lid member **205**. The inlet port **230** and the outlet port **231** disposed in the lid members **205** are connected to adequate places of the pipe conduit of the chemical supply piping system B, as shown in FIG. **1**. The other structures such as the structure of the casing **201**, and the structures for connecting the end portions of the tube **204** to the lid members **205** are identical with those of the heat exchanger **114**. Therefore, like elements are designated by like numbers throughout. Further description is omitted for convenience only and is not limiting.

Referring to FIG. **10**, in the manual de-aerating device **118**, the casing **201** comprises: the tube **204** which is placed in a vertical posture; a pair of upper and lower lid members **205** which hermetically close the upper and lower end portions of the tube **204**, respectively; and the union nuts **206** which fasten the lid members **205** to the upper and lower end portions of the tube **204**, respectively. As a device element, the inlet port **230** is incorporated in the body wall portion **207** of the upper lid member **205**, and an air vent tube **253** and a manual air vent valve **254** are incorporated in the bottom wall portion **209**. The outlet port **231** is disposed in the body wall portion **207** of the lower lid member **205**. In the manual de-aerating device **118**, when the air vent valve **254** is opened, it is possible to remove away, for example, air bubbles in pure water, ultra pure water, or chemical, and which enters from the inlet port **230** of the upper lid member **205**, stagnates in the tube **204**, and then flows out to the outlet port **231** of the lower lid member **205**. The inlet port **230** and the outlet port **231** disposed in the lid members **205** are connected to adequate places of the pipe conduit of the chemical supply piping system B, as shown in FIG. **1**. The other structures such as the structure of the casing **201**, and the structures for connecting the end portions of the tube **204** to the lid members **205** are identical with those of the heat exchanger **114**. Therefore, the identical members and elements are denoted by the same reference numerals, and their description is omitted.

Referring to FIG. **11**, in the automatic de-aerating device **119**, an automatic air vent valve **255** which operates in conjunction with a liquid level sensor **256** disposed outside the tube **204** that is placed in a vertical posture is disposed in the air vent tube **253**. When the liquid level sensor **56** detects the liquid level in the tube **204**, the air vent valve **255** is opened, so that air stagnating in the liquid is discharged. The other configuration and function are identical with those of the manual de-aerating device of FIG. **10**. Therefore, like elements are designated by like numbers throughout. Further description is omitted for convenience only and is not limiting.

Referring to FIG. **12**, in the de-aerating module **120**, as a device element, plural gas permeable tubes **257** made of a foamed fluororesin are passed in a bundled state through the tube **204**, and a de-aerating port **258** is disposed in one of the lid members **205**. The both ends of the gas permeable tubes **257** are communicatingly connected to an inflow pipe **261** and an outflow pipe **262** which are passed through inlet and outlet ports **259** and **260** disposed in the bottom wall portions **209** of the lid members **205** on the ends of the tube **204**, respectively. The inflow pipe **261** and the outflow pipe **262** are connected to adequate places of the pipe conduit of the chemical supply piping system B, as shown in FIG. **1**.

In the de-aerating module, while the pressure of the interior of the tube **204** is reduced through the de-aerating port **258** by a vacuum pump or the like, for example, chemical is passed from the inflow pipe **261** through the gas permeable tubes **257**, and the de-aerating operation is conducted in such a manner that gasses such as air dissolved in the chemical permeate the peripheral walls of the gas permeable tubes **257** to be dissipated into the outside of the gas permeable tubes **257**. The chemical which has undergone the de-aerating process is discharged into the outflow pipe **262**. The other structures such as the structure of the casing **201**, and the structures for connecting the end portions of the tube **204** to the lid members **205** are similar to those of the heat exchanger **114**. Therefore, like elements are designated by like numbers throughout. Further description is omitted for convenience only and is not limiting.

The de-aerating module **120** shown in FIG. **12** can be used also as a gas dissolving device. When the module is used as a gas dissolving device, the de-aerating port **258** is used as a soluble gas supplying port, and, for example, ultra pure water or chemical is passed from the inflow pipe **261** through the gas permeable tubes **257** while a soluble gas such as ozone is supplied under pressure into the tube **204**. The soluble gas in the tube **204** permeates the peripheral wall of the gas permeable tubes **257** to be dissolved into the ultra pure water or chemical in the gas permeable tubes **257**. The to be processed liquid which has undergone the dissolving process is discharged into the outflow pipe **262**.

Other Embodiments of the Casing of the Tube Device

The overall shape of the casing **1** of the tube device can be formed into various shapes including an L-shape shown in FIG. **13**, and a U-shape shown in FIG. **14** in place of the linear pipelike shape in the embodiments described above. In an L-shaped casing **1** shown in FIG. **13**, two or first and second tubes **4A**, **4B**, two or first and second lid members **5A**, **5B**, and one elbow joint member **39** made of a synthetic resin such as a fluororesin are used. In a U-shaped casing **1** shown in FIG. **14**, three or first, second, and third tubes **4A**, **4B**, **4C**, two or first and second lid members **5A**, **5B**, and two or first and second elbow joint members **39A**, **39B** made of a synthetic resin such as a fluororesin are used.

In the L-shaped casing **1** shown in FIG. **13**, the first and second lid members **5A**, **5B** are connected to end portions on one side of the first and second tubes **4A**, **4B** by first union nuts **6**, respectively, and the other ends of the first and second tubes **4A**, **4B** are connected to each other by the single elbow joint member **39** and a pair of second union nuts **40**. In this case, the structure for connecting the first and second lid members **5A**, **5B** to the end portions of the first and second

tubes 4A, 4B is configured in the same manner as that for connecting the end portions of the tube 4 to the lid members 5 in the embodiments described above.

In the joint member 39, connecting ports 41 are opened in the ends so as to perpendicularly communicate with each other, and the internal structures of the connecting ports 41 are identical with those of the receiving portions 8 of the lid members 5. Namely, first to third sealing faces are disposed inside each of the connecting ports 41 of the joint member 39. The first sealing face is configured by a tapered face which is formed inner than the entrance of the connecting port 41, and in which the diameter is gradually increased toward the outer side in the axial direction. The second sealing face is configured by a tapered face in which the diameter is gradually increased toward the outer side in the axial direction. The third sealing face is configured by an annular groove which is formed in an inner portion of the connecting port 41 and in the radially outer side with respect to the first sealing face, and which elongates parallel to the axis. By contrast, inner rings 15 having the same section shape as inner rings 15 in the end portions of the first and second tubes 4A, 4B are pressingly inserted into the other end portions of the first and second tubes 4A, 4B. Therefore, the other end portion of the first tube 4A is connected to the connecting port 41 in the one end of the joint member 39, and that of the second tube 4B is connected to the connecting port 41 in the other end. These connections are conducted by connecting structures which are identical with those for connecting the end portions of the first and second tubes 4A, 4B to the receiving portions 8 of the first and second lid members 5A, 5B. A fluid tube 3 is perpendicularly bent inside the joint member 39.

In the U-shaped casing 1 shown in FIG. 14, the first and second lid members 5A, 5B are connected to end portions on one side of the first and second tubes 4A, 4B by first union nuts 6, and the third tube 4C is connected between the other end portions of the first and second tubes 4A, 4B by the two elbow joint members 39 and a pair of second union nuts 40. In this case also, the structure for connecting the receiving portions 8 of the first and second lid members 5A, 5B to the end portions of the first and second tubes 4A, 4B is configured in the same manner as that for connecting the end portions of the tube 4 to the lid members 5 in the embodiments described above. The structure for connecting the connecting ports 41 of the joint members 39 to the other ends of the first and second tubes 4A, 4B, and that for connecting the connecting ports 41 of the joint members 39 to the both ends of the third tube 4C are identical with that for connecting the end portions of the first and second tubes 4A, 4B to the receiving portions 8 of the first and second lid members 5A, 5B. The fluid tube 3 is perpendicularly bent inside the joint members 39.

Alternatively, the casing 1 may be formed into a shape in which the L-shaped casing 1 of FIG. 13 is combined with the U-shaped casing 1 of FIG. 14.

When the casing 1 of the tube device is formed into an L-shape, a U-shape, or the like as described above, it is possible to build a compact piping system in which a dead space of pipes is effectively used. The device can be advantageously formed into a shape which can satisfy a request for modifying a piping system, such as that for newly installing a tube device in an existing piping system.

Other Embodiments of the Sealing Portion

In each of the sealing portions formed between the end portions of the tube 4 and the receiving portions 8 of the lid members 5, as in the embodiment shown in FIG. 3, the sealing property can be improved more surely by, in addition to the first and second sealing portions 19, 21, further providing the third sealing portion 23 due to the cylindrical portion 24 of the inner ring 15 and the annular groove 13 of the lid member 5. The structure of the sealing portion is not restricted to this. As shown in FIG. 15, for example, a structure may be employed in which only the first and second sealing portions 19, 21 are formed, and the third sealing portion 23 is omitted. In the structure, specifically, the annular groove 13 is not formed in an inner portion of the lid member 5, and the cylindrical portion 24 is not disposed in the inner ring 15. In this case, the first sealing face 10 disposed in an inner portion of the lid member 5 is configured by a tapered face in which the diameter is gradually reduced so as to intersect with the axis C in a direction opposite to that of the second sealing face 11, or toward the outer side in the direction of the axis C.

Alternatively, as shown in FIG. 16, a sealing face 42 formed by a tapered face in which the diameter is larger than the inner diameter of the tube 4 is formed on the outer periphery of the end portion on the tip end side of the receiving portion 8 of the lid member 5, and an external thread portion 14 in which the diameter is larger than the outer diameter of the sealing face 42 is formed in the outer periphery in rear of the sealing face 42. A flaring process is applied to the end portion of the tube 4 to form a large diameter portion 43. The large diameter portion 43 in the end portion of the tube 4 is pressingly fitted onto the sealing face 42 of the lid member 5. The union nut 6 fitted onto the tube 4 is then screwed and fastened to the external thread portion 14 of the lid member 5, so that the pressing edge 26*a* of the annular flange 26 of the union nut 6 butts against the outer side of the tube 4 to axially press the inner peripheral face of the large diameter portion 43 against the sealing face 42 of the receiving portion 8 to be closely contacted therewith, whereby a sealing portion 44 is formed.

Alternatively, a sealing structure may be configured as shown in FIG. 17. An inner ring 45 which is made of made of a synthetic resin such as a fluororesin, and which has an arcuate section shape is pressingly inserted into the end portion of the tube 4 to increase the diameter of the end portion, thereby expanding the end portion so as to have a mountain-like section shape. A union nut 6 screwed to an external thread portion 14 of the lid member 5 is screwingly advanced to firmly fasten the end portion. As a result, the end portion of the tube 4 is pressed together with the inner ring 45 against a tapered sealing face 46 disposed on the inner periphery of the receiving portion 8 of the lid member 5, to be closely contacted therewith, thereby forming a sealing portion 47.

Alternatively, a sealing structure may be configured as shown in FIG. 18. An outer ring 48 is fitted onto the end portion of the tube 4. The terminal portion of the tube 4 is folded back onto the outer face of the outer ring 48. A union nut 6 screwed to an external thread portion 14 of the lid member 5 is screwingly advanced to firmly fasten the terminal portion. As a result, the end portion of the tube 4 is pressed together with the outer ring 48 against a tapered sealing face 49 in the receiving portion 8 of the lid member 5, to be closely contacted therewith, thereby forming a sealing portion 50.

It is a matter of course that the invention can be similarly applied also to various piping systems other than a chemical supply piping system in an apparatus for producing semiconductor devices.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover

modifications within the spirit and scope of the present invention as defined by the appended claims.

We claim:

1. A tube device including a casing, and a device element which is placed in said casing, wherein said casing comprises:

a tube made of a synthetic resin;

a pair of lid members which are made of a synthetic resin;

a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of said tube, and which are screwed to end portions of said lid members having receiving ports, respectively; and

a sealing portion which is formed in at least one place for each of said end portions of said tube by closely contacting said end portion of said tube with a sealing face of a corresponding one of said lid members, said end portion of said tube and said sealing face of said lid member being closely contacted with each other by causing a corresponding one of said union nuts to press said tube from an outside of said tube, said corresponding one of said union nuts fastening said end portion of said lid member by screw advancement toward said end portion of said lid member, thereby pressing said tube from the outside of said tube,

wherein said device element is a heat exchange tube which is made of a synthetic resin, and in which an outer periphery is surrounded by said tube made of synthetic resin and connecting portions which are disposed on said pair of lid members made of a synthetic resin, and to which outlet ports of said heat exchange tube, and pipes for introducing and discharging a fluid that is passed between an inner side of said casing and an outer side of said heat exchange tube are connected, respectively,

wherein an inner ring is formed in each of said end portions of said tube, said inner ring having: a press-insertion portion which is pressingly inserted into said end portion of said tube to increase a diameter of said end portion, thereby expanding said end portion so as to have a protruding shape; and a projection portion which projects from said end portion of said tube, and

wherein said sealing portion is formed by close contact between: a sealing face configured as a tapered face which is formed inward of an entrance of a receiving portion of said lid member, and in which a diameter is gradually increased toward an outer side in an axial direction of said lid member; and a projection end face formed by a tapered face which is formed in a tip end of said projection portion of said inner ring.

2. A tube device including a casing, and a device element which is placed in said casing, wherein said casing comprises:

a tube made of a synthetic resin;

a pair of lid members which are made of a synthetic resin;

a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of said tube, and which are screwed to end portions of said lid members having receiving ports, respectively; and

a sealing portion which is formed in at least one place for each of said end portions of said tube by closely contacting said end portion of said tube with a sealing face of a corresponding one of said lid members, said end portion of said tube and said sealing face of said lid member being closely contacted with each other by causing a corresponding one of said union nuts to press said tube from an outside of said tube, said corresponding one of said union nuts fastening said end portion of said lid member by screw advancement toward said end portion of said lid member, thereby pressing said tube from the outside of said tube,

wherein said device element is a heat exchange tube which is made of a synthetic resin, and in which an outer periphery is surrounded by said tube made of synthetic resin and connecting portions which are disposed on said pair of lid members made of a synthetic resin, and to which outlet ports of said heat exchange tube, and pipes for introducing and discharging a fluid that is passed between an inner side of said casing and an outer side of said heat exchange tube are connected, respectively,

wherein an inner ring is formed in each of said end portions of said tube, said inner ring having: a press-insertion portion which is pressingly inserted into said end portion of said tube to increase a diameter of said end portion, thereby expanding said end portion so as to have a protruding shape; and a projection portion which projects from said end portion of said tube, and

wherein said sealing portion is formed by pressingly holding said end portion of said tube in an inclined state between: a sealing face which is formed in an entrance of a receiving portion of said lid member by a tapered face intersecting with an axis of said lid member, and an inward tapered face which is formed on an inclined face of said press-insertion portion of said inner ring.

3. A tube device including a casing, and a device element which is placed in said casing, wherein said casing comprises:

a tube made of a synthetic resin;

a pair of lid members which are made of a synthetic resin;

a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of said tube, and which are screwed to end portions of said lid members having receiving ports, respectively; and

a sealing portion which is formed in at least one place for each of said end portions of said tube by closely contacting said end portion of said tube with a sealing face of a corresponding one of said lid members, said end portion of said tube and said sealing face of said lid member being closely contacted with each other by causing a corresponding one of said union nuts to press said tube from an outside of said tube, said corresponding one of said union nuts fastening said end portion of said lid member by screw advancement toward said end portion of said lid member, thereby pressing said tube from the outside of said tube,

wherein said device element is a heat exchange tube which is made of a synthetic resin, and in which an outer periphery is surrounded by said tube made of synthetic resin and connecting portions which are disposed on said pair of lid members made of a synthetic resin, and to which outlet ports of said heat exchange tube, and pipes for introducing and discharging a fluid that is passed between an inner side of said casing and an outer side of said, heat exchange tube are connected, respectively,

wherein an inner ring is formed in each of said end portions of said tube, said inner ring having: a press-insertion portion which is pressingly inserted into said end portion of said tube to increase a diameter of said end portion, thereby expanding said end portion so as to have a protruding shape; and a projection portion which projects from said end portion of said tube, and

wherein said tube device comprises a plurality of said sealing portions for each of said end portions of said tube, said sealing portions being:

a sealing portion formed by close contact between: a sealing face configured as by ataperedfacewhichisformedinwardofanentranceofareceivingportionofsaidlidmember, and in which a diameter is gradually increased toward an outer side in an axial

direction of said lid member; and a projection end face formed by a tapered face which is formed in a tip end of said projection portion of said inner ring; and

a sealing portion formed by pressingly holding said end portion of said tube in an inclined state between: a sealing face which is formed in an entrance of said receiving portion of said lid member by a tapered face intersecting with an axis of said lid member; and an inward tapered face which is formed on an inclined face of said press-insertion portion of said inner ring.

4. A tube device including a casing, and a device element which is placed in said casing, wherein said casing comprises:

a tube made of a synthetic resin;

a pair of lid members which are made of a synthetic resin;

a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of said tube, and which are screwed to end portions of said lid members having receiving ports, respectively; and

a sealing portion which is formed in at least one place for each of said end portions of said tube by closely contacting said end portion of said tube with a sealing face of a corresponding one of said lid members, said end portion of said tube and said sealing face of said lid member being closely contacted with each other by causing a corresponding one of said union nuts to press said tube from an outside of said tube, said corresponding one of said union nuts fastening said end portion of said lid member by screw advancement toward said end portion of said lid member, thereby pressing said tube from the outside of said tube,

wherein said device element is a heat exchange tube which is made of a synthetic resin, and in which an outer periphery is surrounded by said tube made of synthetic resin and connecting portions which are disposed on said pair of lid members made of a synthetic resin, and to which outlet ports of said heat exchange tube, and pipes for introducing and discharging a fluid that is passed between an inner side of said casing and an outer side of said heat exchange tube are connected, respectively,

wherein an inner ring is formed in each of said end portions of said tube, said inner ring having: a press-insertion portion which is pressingly inserted into said end portion of said tube to increase a diameter of said end portion, thereby expanding said end portion so as to have a protruding shape; and a projection portion which projects from said end portion of said tube, and

wherein said tube device comprises a plurality of said sealing portions for each of said end portions of said tube, said sealing portions being:

a sealing portion formed by close contact between: a sealing face configured as a tapered face which is formed inward of an entrance of a receiving portion of said lid member, and in which a diameter is gradually increased toward an outer side in an axial direction of said lid member; and a projection end face formed by a tapered face which is formed in a tip end of said projection portion of said inner ring; and

wherein another sealing portion is formed by fitting a cylindrical portion which is formed in a tip end of said projection portion of said inner ring, into an annular groove which is formed in a radial outer side with respect to said sealing face that is formed in an inner portion of said receiving portion of said lid member, said annular groove being elongated parallel to an axis of said lid member.

5. A tube device including a casing, and a device element which is placed in said casing, wherein said casing comprises:

a tube made of a synthetic resin;

a pair of lid members which are made of a synthetic resin;

a pair of union nuts which are made of a synthetic resin, which are fitted onto one and other end portions of said tube, and which are screwed to end portions of said lid members having receiving ports, respectively; and

a sealing portion which is formed in at least one place for each of said end portions of said tube by closely contacting said end portion of said tube with a sealing face of a corresponding one of said lid members, said end portion of said tube and said sealing face of said lid member being closely contacted with each other by causing a corresponding one of said union nuts to press said tube from an outside of said tube, said corresponding one of said union nuts fastening said end portion of said lid member by screw advancement toward said end portion of said lid member, thereby pressing said tube from the outside of said tube,

wherein said device element is a heat exchange tube which is made of a synthetic resin, and in which an outer periphery is surrounded by said tube made of synthetic resin and connecting portions which are disposed on said pair of lid members made of a synthetic resin, and to which outlet ports of said heat exchange tube, and pipes for introducing and discharging a fluid that is passed between an inner side of said casing and an outer side of said heat exchange tube are connected, respectively,

wherein an inner ring is formed in each of said end portions of said tube, said inner ring having: a press-insertion portion which is pressingly inserted into said end portion of said tube to increase a diameter of said end portion, thereby expanding said end portion so as to have a protruding shape; and said inner ring further having a projection portion which projects from said end portion of said tube, and

wherein said tube device comprises a plurality of said sealing portions for each of said end portions of said tube, said sealing portions comprising:

a sealing portion formed by pressingly holding said end portion of said tube in an inclined state between: a sealing face which is formed in an entrance of a receiving portion of said lid member by a tapered face intersecting with an axis of said lid member; and an inward tapered face which is formed on an inclined face of said press-insertion portion of said inner ring; and

wherein another sealing portion is formed by fitting a cylindrical portion which is formed in a tip end of said projection portion of said inner ring, into an annular groove which is formed in a radial outer side with respect to said sealing face that is formed in an inner portion of said receiving portion of said lid member, said annular groove being elongated parallel to an axis of said lid member.

* * * * *

United States Patent [19]

Hirota et al.

[11] **Patent Number: 4,740,434**

[45] **Date of Patent: Apr. 26, 1988**

[54] **SURFACE TREATED ELECTRODES APPLICABLE TO ZINC-HALOGEN SECONDARY BATTERIES**

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[73] Assignee: **Kabushiki Kaisha Meidensha**, Tokyo, Japan

[21] Appl. No.: **935,343**

[22] Filed: **Nov. 26, 1986**

[30] **Foreign Application Priority Data**

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Mar. 4, 1986 [JP] Japan 61-45435

[51] **Int. Cl.**^{4} **H01M 4/96**

[52] **U.S. Cl.** **429/105**; 429/199; 429/209

[58] **Field of Search** 429/101, 105, 199, 209, 429/42, 44, 218

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Primary Examiner—Anthony Skapars

Attorney, Agent, or Firm—Bachman & LaPointe

[57] **ABSTRACT**

A surface treated electrode applicable to an electrode of a zinc-halogen secondary battery, etc. The surface plastic electrode includes (a) an electrically conductive electrode substrate material; and (b) a surface treatment material on the electrode substrate material, the surface treatment material being made of a phenol resin series activated charcoal fiber satisfying predetermined characteristic such that a weight per unit area substantially equal to 100 g/m^2 or more, pore diameter having a distribution peak in a range from 1.5 nm to 3.5 nm, a surface area of a part substantially equal to or more than 30 m^2/g occupied by pores whose diameters range from 1 nm to 11 nm, a whole relative surface area of the entire pore diameter ranging substantially equal to or more than 1500 m^2/g, a tensile strength substantially equal to or more than 294 MPa (30 kg/mm^2) and a tensile modulus substantially equal to or less than 14710.5 MPa (1500 kg/mm^2). The conductive electrode substrate material is, for example, carbon plastic, glassy carbon, or Carbon-Carbon (C/C) composite. In the case of the C/C composite electrode substrate material, an ion exchange fiber is adhered onto one surface of the C/C composite electrode substrate material to form a three-layer type electrode.

20 Claims, 3 Drawing Sheets

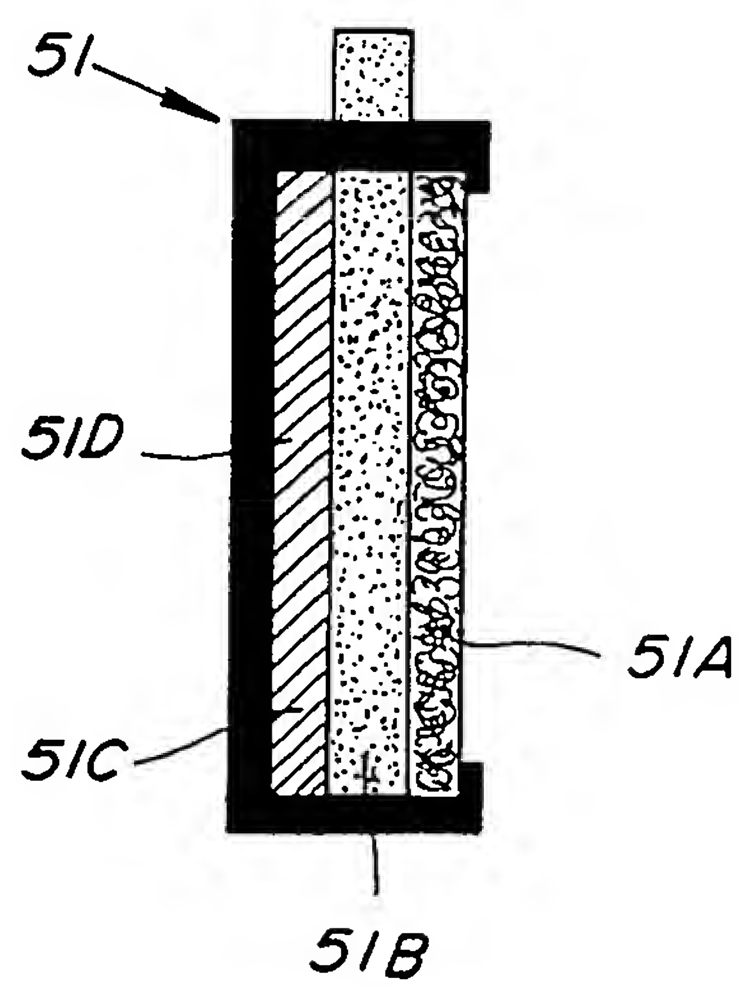


FIG. 1

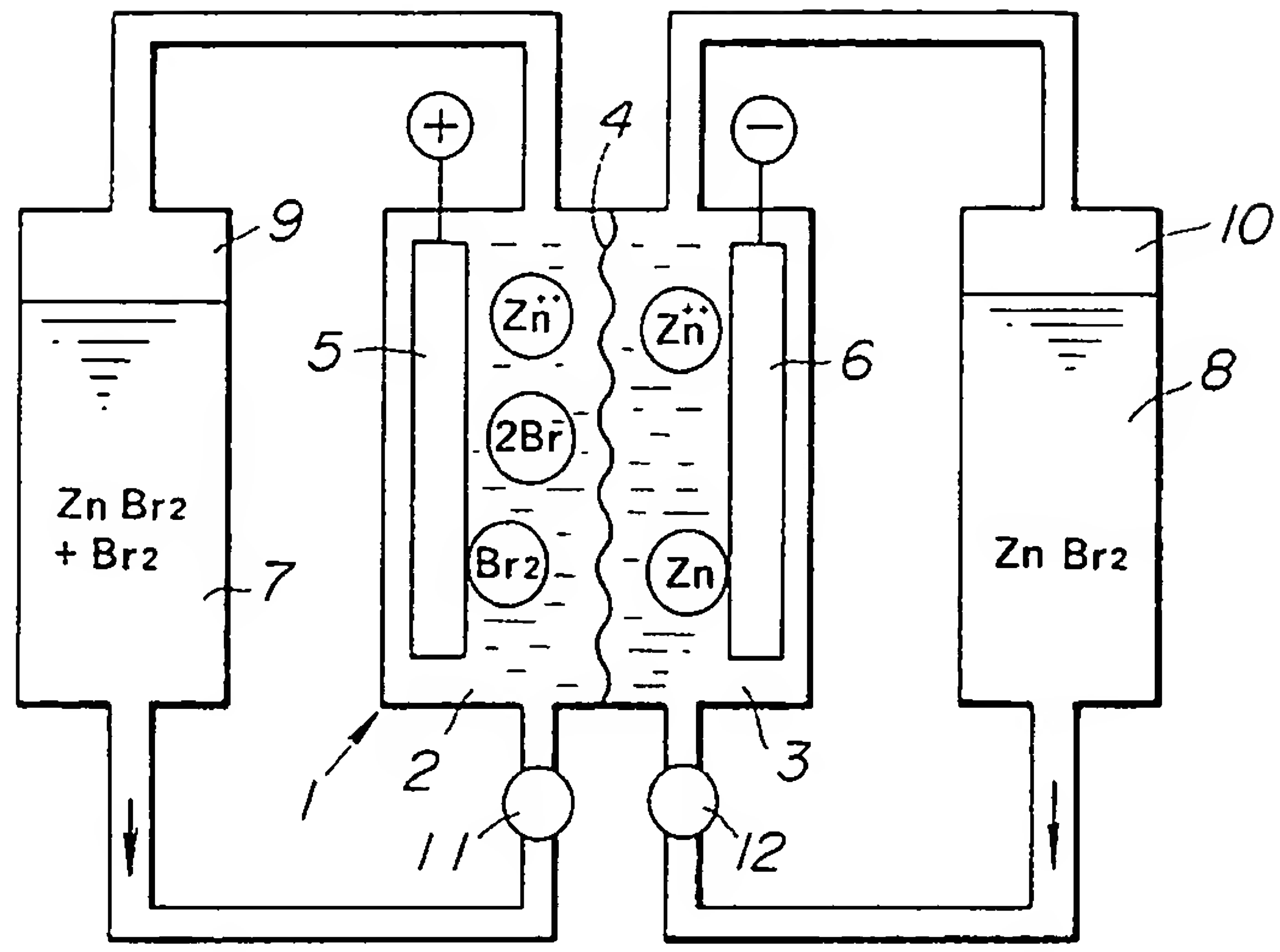

4
9
10
5
6
8
Zn Br2
+ Br2
7
Zn Br2
1
2
3
11
12

FIG. 4

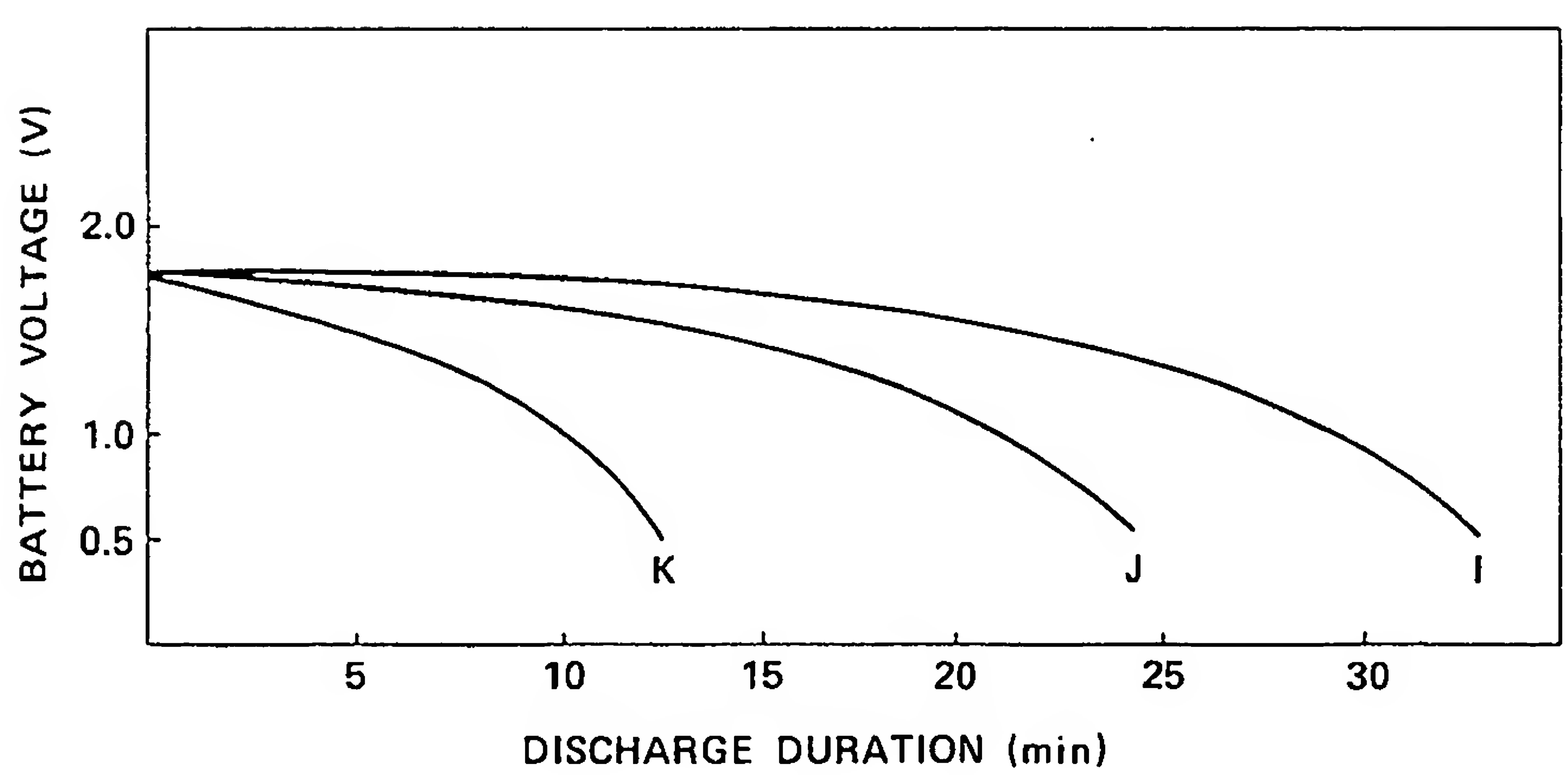

BATTERY VOLTAGE (V)
2.0
1.0
0.5
K
J
I
5
10
15
20
25
30
DISCHARGE DURATION (min)

FIG. 2

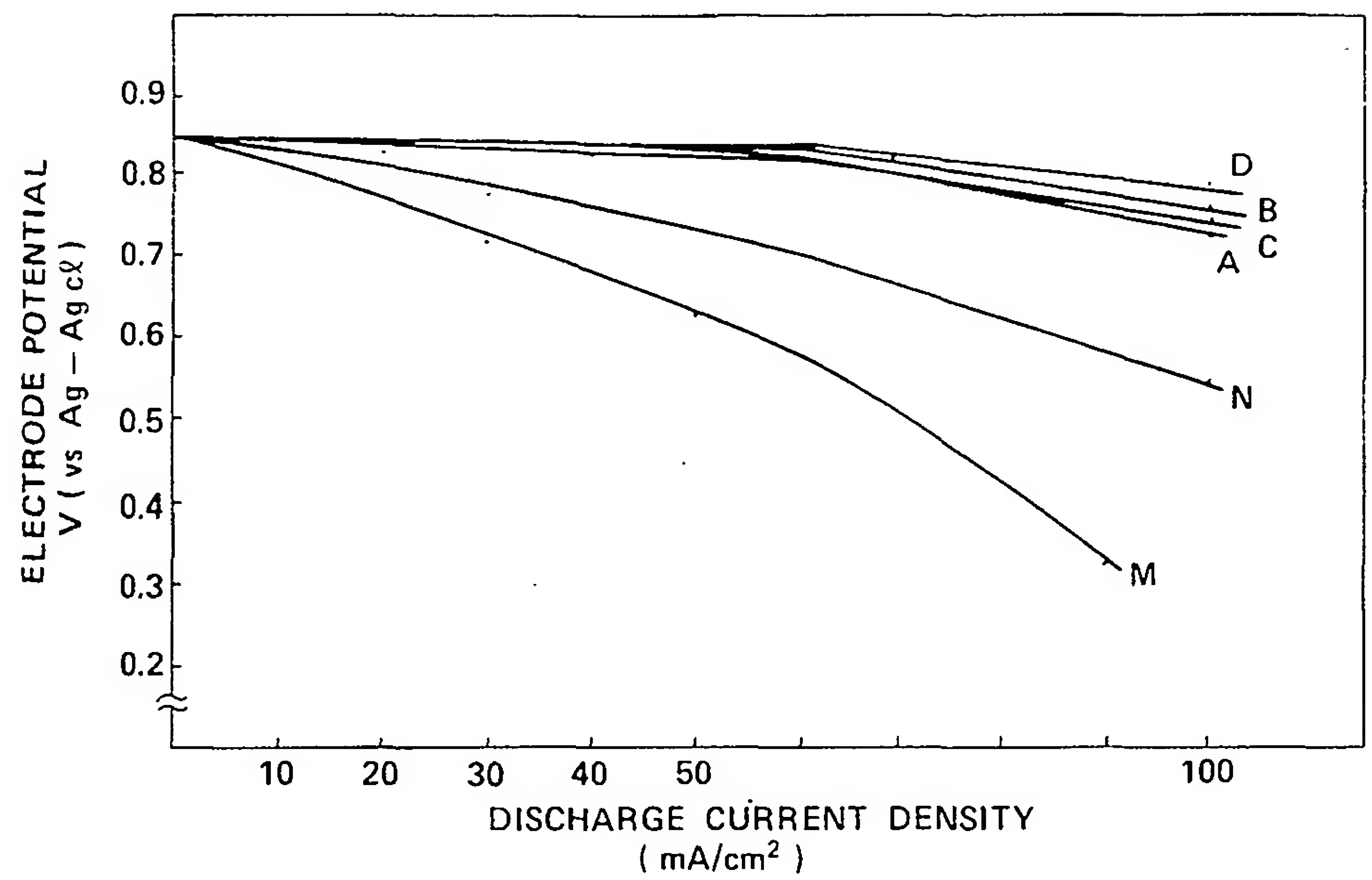

ELECTRODE POTENTIAL
V (vs Ag – Ag cℓ)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
10
20
30
40
50
100
DISCHARGE CURRENT DENSITY
(mA/cm²)
D
B
C
A
N
M

FIG. 3

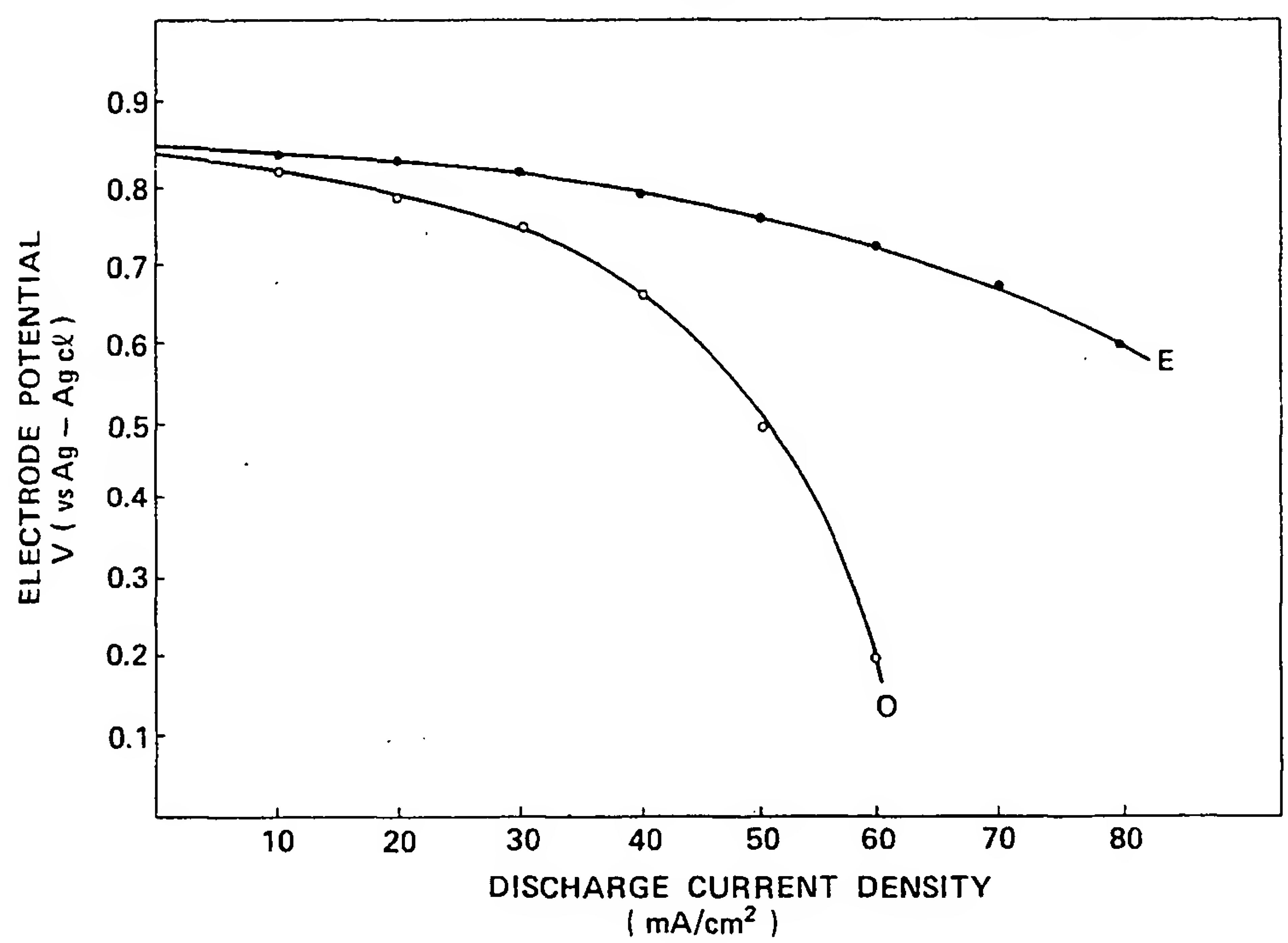

ELECTRODE POTENTIAL
V (vs Ag – Ag cℓ)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10
20
30
40
50
60
70
80
DISCHARGE CURRENT DENSITY
(mA/cm²)
E
O

FIG. 5

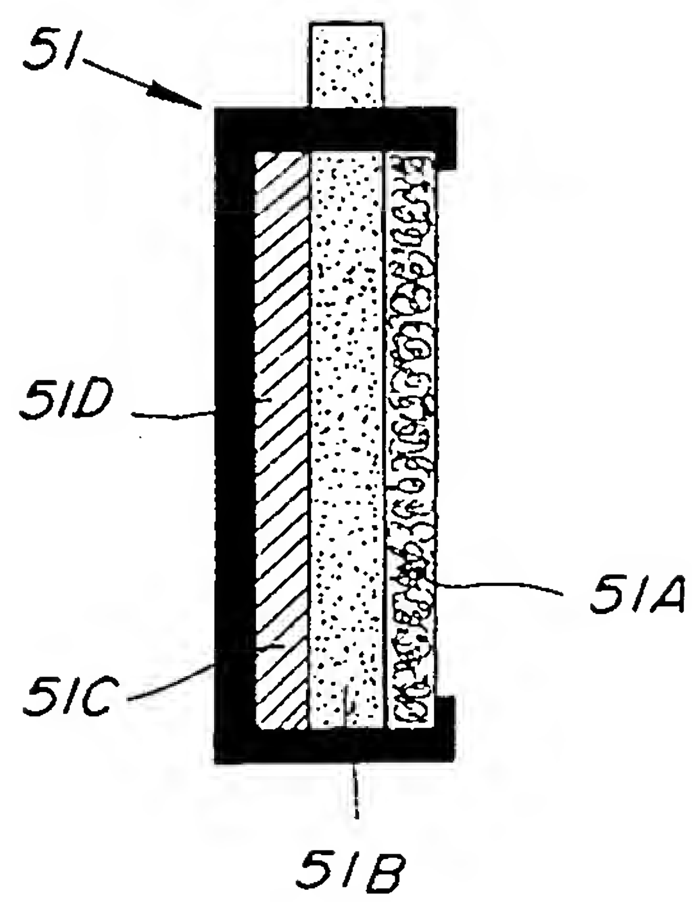


FIG. 6

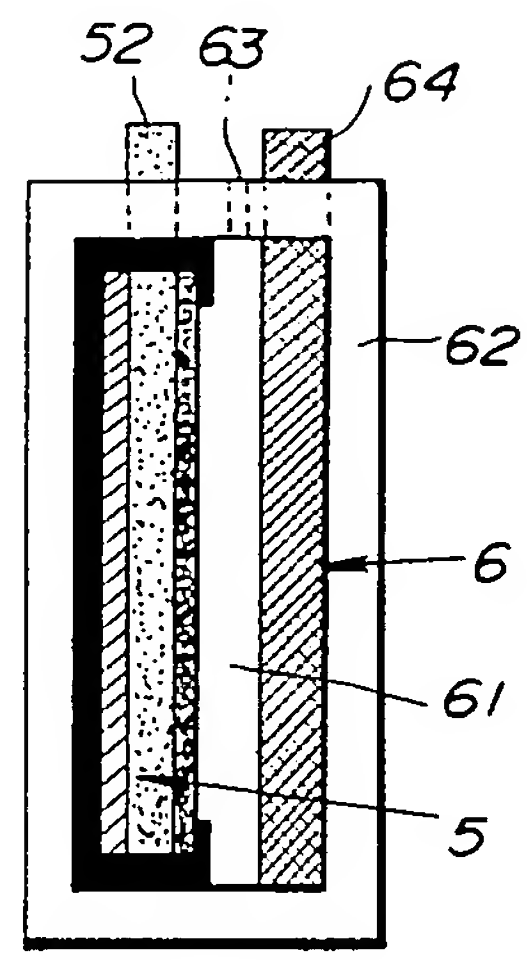
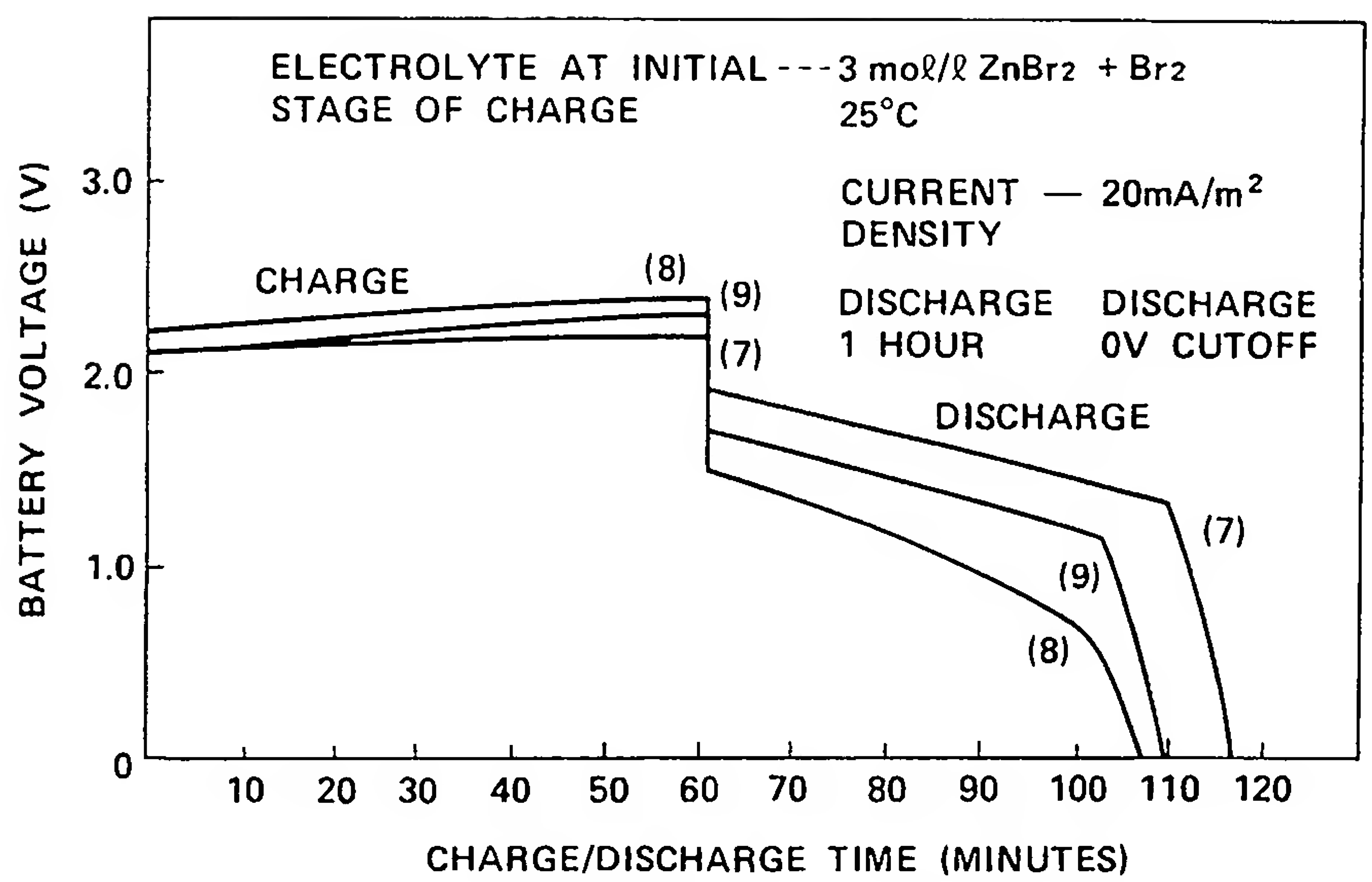


FIG. 7



SURFACE TREATED ELECTRODES APPLICABLE TO ZINC-HALOGEN SECONDARY BATTERIES

BACKGROUND OF THE INVENTION

The present invention relates to surface treated electrodes particularly applicable to positive electrodes of zinc-halogen secondary batteries such as zinc-bromine secondary batteries and so on. The present invention particularly relates to the surface treated electrodes in which active carbon (activated charcoal) fibers whose originating raw materials are phenol formaldehydes are adhered onto conductive electrode substrates, for example, under mechanical pressure and heat or attached thereto.

Carbon fibers are effective materials as materials for surface treatments of positive electrodes in zinc-halogen secondary batteries. An electrode under a surface treatment has conventionally been used with such a carbon fiber as belonging to cloth-formed rayon and acryl series adhered onto a surface of a carbon plastic (C.P) under mechanical pressure and heat.

However, such carbon fibers as belonging to the rayon and acryl series in the above-described cloth forms have problems in their activation processing methods so that sufficient activations in zinc-halogen secondary batteries, especially in zinc-bromine secondary batteries cannot yet be achieved.

That is to say, since an area of a part occupied by pores having diameters of 1 to 11 nm required for a positive electrode reaction in the above-described electric secondary batteries is not yet formed in a sufficient quantity to carry out the positive electrode reaction in the above-described carbon fibers, an over voltage becomes remarkably large when the charge and discharge operations are carried out especially in high current densities equal to or more than 60 mA/cm^2.

In addition, since the above-described carbon fibers have small weights per unit area in a unit of sheet (referred to as a METSUKE in Japanese and this unit is g/m^2 in Japan and lb/yd^2 in England), are thin in thickness, and weak in mechanical strength such as tensile and bending strengths, they cannot withstand a high mechanical pressure under which they are adhered onto the carbon plastics (C.P) by heat pressing operation, many such carbon fibers are destroyed to become powders and to become short length fibers during this process so that they drop off electrode surfaces. Consequently, electrochemical performances of the zinc-bromine secondary batteries will greatly be reduced.

SUMMARY OF THE INVENTION

With the above-described problems in mind, it is an object of the present invention to provide surface treated electrodes which improve battery characteristics in batteries whose electrodes according to the present invention are used and have a high mechanical strength.

It is another object of the present invention to provide the surface treated electrodes applicable to positive electrodes of zinc-halogen secondary batteries such as zinc-bromine secondary batteries which improve the battery characteristics in the zinc-halogen secondary batteries and have the high mechancal strength, both required for the zinc-halogen secondary batteries.

The above-described objects can be achieved by providing a surface treated electrode, comprising: (a) an electrically conductive material constituting a substrate

of the electrode; and (b) a surface treatment material on the conductive electrode substrate material, the surface treatment material being made of phenol resin series activated charcoal fiber satisfying predetermined characteristics.

The predetermined characteristics are specifically a weight per unit area of 100 g/m^2 or more, pore diameters having a distribution peak substantially in a range from 1.5 nm to 3.5 nm, a surface area of a part equal to or more than 30 m^2/g occupied by pores whose diameters substantially range from 1 nm to 11 nm, a whole surface area of pore diameter range equal to or more than 1500 m^2/g, a tensile strength substantially equal to or more than 294 MPa (30 kg/mm^2), and a tensile modulus substantially equal to or less than 14710.5 MPa (1500 kg/mm^2).

The invention performed experiments on battery characteristics using various kinds of activated charcoal fibers for carrying out surface treatments on electrode substrates such as carbon plastic electrode substrates. The experiments used an activated charcoal fiber belonging to phenol resin series (novoloid of a phenol formaldehyde) adhered onto a conductive electrode substrate surface. The electrode whose surface is treated in this way is used as a positive electrode of the zinc-halogen secondary battery and it is more advantageous in its battery characteristics and mechanical strength than the case where the cloth formed activated charcoal fibers such as those belonging to the rayon, cellulose, and acryl series are used as surface treatment materials of electrode substrates and they are used for positive electrodes of the zinc-halogen secondary batteries.

The present invention is also applicable to electrodes of other zinc-halogen secondary battery.

The activated charcoal fibers in resin series are manufactured, e.g., by melt spinning phenol resins (novoloids of phenol formaldehyde) and thereafter activating and sintering them under vaporized water.

The activated charcoal fibers whose originating raw materials are phenol formaldehydes are, for example, kynol activated charcoal fibers manufactured by Nihon Kynol Company Limtied, Cloth-ACC series and Felt ACN series.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a basic construction of a zinc-bromine secondary battery to which a surface treated electrode according to the present invention is applicable.

FIG. 2 is a characteristic graph representing a relationship between an electrode potential and discharge current density in the surface treated carbon plastic electrode in a first preferred embodiment according to the present invention.

FIG. 3 is a characteristic graph representing the relationship between the electrode potential and discharge current density in the surface treated electrode in a second preferred embodiment according to the present invention.

FIG. 4 is a characteristic graph representing the relationship between a discharge duration and battery voltage of the surface treated electrode in a third preferred embodiment according to the present invention.

FIG. 5 is a cross sectional view of an electrode having a three-layer construction in the surface treated electrode in a fourth preferred embodiment.

FIG. 6 is a cross sectional view of a liquid static type secondary battery in a fifth preferred embodiment.

FIG. 7 is a characteristic graph representing a relationship between a charge-discharge duration and battery voltage.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will hereinafter be made to the drawings in order to facilitate understanding of the present invention. Before explaining preferred embodiments according to the present invention, a construction of a zinc-bromine secondary battery will briefly be described.

FIG. 1 shows a basic construction of a zinc-bromine secondary battery to which a surface treated carbon plastic electrode according to the present invention is applicable.

As shown in FIG. 1, a positive electrode 5 and a negative electrode 6 are separated mutually by a separation member constituted by, e.g., a microporous sheet or ion exchange membrane, denoted by numeral 4, for providing independent electrochemical reactions in each of positive and negative electrode chambers 2, 3. Positive and negative electrolytes for both positive and negative electrode chambers 2, 3 are stored within external electrolyte storage tanks 7, 8, respectively. When charge and discharge of a secondary unit cell generally denoted by 1 are carried out, each electrolyte is supplied to the corresponding electrode chamber 2, 3 by means of corresponding pumps 11, 12 intervened in a lower conduit disposed between the corresponding storage tanks 7, 8 and electrode chambers 2, 3. As the electrolyte for the positive electrode 5, e.g., an aqueous solution of $ZnBr_2$ plus bromine molecule (Br_2) and bromine complexing agent are used. The addition of the complexing agent contributes the bromine molecule in the positive electrolyte to be changed to a low vapor pressure, low water soluble oily bromine complex.

When the discharge action is carried out, $ZnBr_2$ solution including bromine complex is introduced into the positive electrode chamber 2 by means of the pump 11. In the positive electrode 5, bromine complex is reduced to Br^- ion. On the other hand, in the negative electrode 6 on which zinc is electrodeposited, $ZnBr_2$ solution is introduced by means of the pump 12 and zinc is oxidized to Zn^{++} ion. When the charge action is carried out, bromine molecule is generated in the positive electrode 5 ($2Br^- \rightarrow Br_2 + 2e^-$) and zinc is electrodeposited in the negative electrode 6 ($Zn^{++} + 2e^- \rightarrow Zn$). The electrochemical reaction in the zinc-bromine secondary battery is expressed as follows:

$$Zn + Br_2 \underset{\text{CHARGE}}{\overset{\text{DISCHARGE}}{\rightleftarrows}} ZnBr_2$$

The construction and reaction of the zinc-bromine secondary battery are described by a U.S. Pat. No. 4,461,817 published on July 24, 1984 and U.S. Pat. No. 4,510,218 published on Apr. 9, 1985. The U.S. Patent documents are hereby incorporated by reference.

Before explaining preferred embodiments, Table 1 shows lists of article numbers of activated charcoal fiber sheets used in the preferred embodiments and their characteristics.

TABLE 1

Symbols of Electrodes	characteristics of eleven sheets (A through G and M through Q) of positive electrode surface treatment materials: Surface Treatment Materials	Weight per unit area (g/m²)	Thickness (mm)	Surface area (m²/g)	pore diameter of fiber (nm)	form
A E	ACC507-15 Nihon Kynol Co., Ltd.	135	0.53	1500	1.5-3.5	cloth
B	ACC507-20 Nihon Kynol Co., Ltd.	115	0.44	2000	1.5-3.5	cloth
C	ACN210-15 Nihon Kynol Co., Ltd.	120	2.10	1500	1.5-3.5	felt
D	ACN210-20 Nihon Kynol Co., Ltd.	100	2.20	2000	1.5-3.5	felt
G	ACC509-20 Nihon Kynol Co., Ltd.	175	0.60	2000	1.5-3.5	cloth
M	KF-M-203 Toyobo Inc.	44	0.25	1500	1.5-2.0	knit
N, O, Q	KF-M-303 Toyobo Inc.	82	0.48	1600	1.5-2.0	cloth
P	FE-400 Toho Rayon Inc.	60	—	1100	0.8-2.0	felt

FIRST PREFERRED EMBODIMENT

The inventors investigated respective discharge characteristics of the plurality of zinc-halogen secondary batteries using the same electrolytes, each having a concentration of 3 mol/l$ZnBr_2 + Br_2$ (0.4 to 1.0 mol/l). Their positive electrodes were formed of surface treated carbon plastic (C.P) electrodes, each having a weight ratio of P.E. : C.B (P.E denotes a polyethylene and C.B denotes a carbon black) being 100:50. At this time, four kinds of activated charcoal fiber sheets selected from among phenol resin series activated charcoal fibers (manufactured by Nippon Kynol Company Limited) shown in Table 1 and two kinds of activated charcoal fibers selected from among rayon series activated charcoal fiber sheets (manufactured by Toyobo Incorporation) shown in Table 1 were adhered as surface treatment materials onto the carbon plastic electrodes under mechanical pressure and heat, respectively. In this way, the six surface treated carbon plastic electrodes A through D, M and N were formed.

In addition, FIG. 2 shows the experimental results of discharge characteristics of the carbon plastic electrodes (A through D, M and N) whose surfaces were respectively treated with these activated charcoal fibers.

As appreciated from FIG. 2, the electrodes A through D treated with the phenol resin series activated charcoal fiber sheets have better discharge characteristics than the electrodes M and N treated with the two kinds of rayon series activated charcoal fibers.

Especially, although the activated charcoal fiber sheet of article number KF-M-303 in the cloth form used for the electrode N was substantially the same as

the phenol resin series activated charcoal fiber sheet of ACC507-15 used in the electrode A in both relative surface area (m^2/g) and cloth form as shown in Table 1, the discharge characteristics thereof became considerably lower than ACC507-15 as shown in FIG. 2. This may be caused by differences in the weight per unit area in the unit of fiber and in thickness as estimated from Table 1.

SECOND PREFERRED EMBODIMENT

The inventors prepared two different carbon plastic electrodes E and O from the same carbon plastics (C.P.U) [each having a weight ratio of P.E (polyethylene)/C.B. (carbon black)/G (graphite)=50/15/35]. For their surface treatment materials, two kinds of activated charcoal fibers, i.e., ACC507-15(E) and KF-M-303(O) were selected from among six kinds of activated charcoal fibers which were used in the first preferred embodiment and adhered onto the respective surfaces of the carbon plastics under pressure of 5.88 MPa (60 kg/cm^2) and temperature of 140° C. for three minutes using a metallic die used for manufacturing the electrodes.

Table 2 shows several characteristics of the above-described electrodes E and O.

FIG. 3 shows respective discharge characteristics thereof. It is noted that requirements for the electrolyte are the same as those in the case of the first preferred embodiment.

TABLE 2

	Characteristics of electrode E and electrode O			
	Thickness*3 (mm)	Relative Resistance (Ω-cm)	Surface*4 Area (m^2/g)	Tensile*5 Strength (kg/mm^2)
E*1	1.50	0.168	995	315
O*2	1.33	0.154	330	316

*1 ACC507-15 is used for the surface treatment material of the electrode
*2 KF-M-303 is used for the surface treatment material of the electrode
*3 The C.P.U of the electrode substrate has a thickness of about 1.0 mm
*4 Relative surface area including electrode substrate (B.E.T (Brunauer, Emmett, Teller) method)
*5 kg/mm^2 = 9.807 MPa

As appreciated from Table 2, although there is little difference between the electrodes E and O in their thickness and relative resistance values, the electrode E is larger than the electrode O in their surface areas including the electrode substrates. This may be caused by their weights per unit area and mechanical strengths (tensile strength) of the activated charcoal fibers of the surface treatment materials and by the fact that the electrode E using the activated charcoal fiber of (E) ACC507-15 having both greater weight per unit area and higher mechanical strength (tensile strength) is sealed to the electrode surface with little destruction of fibers during the pressure and heat adhering process.

THIRD PREFERRED EMBODIMENTS

In this embodiment, the inventors prepared the three unit cell type zinc-bromine secondary batteries each having an interelectrode distance of 10 mm without separation member and constituted by the respective positive electrodes of B, D, and N used in the first preferred embodiment, negative electrodes of Zn plates, and electrolytes of 3 mol/l $ZnBr_2$. In addition, the secondary batteries have charged for one hour with the current density of 20 mA/cm^2. After the charge operation, each electrolyte was renewed with 3 mol/l $ZnBr_2$. Then the secondary batteries were discharged with the same current density to discuss holding capacities of bromine of the respective positive electrodes. The results of the holding capacities are shown in FIG. 4.

FIG. 4 shows change patterns of discharge voltages with respect to a discharge duration in minutes.

As shown in FIG. 4, one of the batteries I in which ACN210-20 was used as the positive electrode surface treatment material of the electrode D indicated a higher discharge voltage and a longer discharge duration than the battery J in which ACC507-20 was used as the positive electrode surface treatment material of the electrode B. In addition, the battery J had a better characteristic than the battery K in which KF-M-303 was used as the positive electrode surface treatment material of the electrode N.

Consequently, as the surface area of the activated carbon fiber sheet is increased, the activated carbon fibers indicate better characteristics.

Next, other electrodes in which the activated charcoal fibers made of novoloid fibers of phenol resin series as the originating raw materials are surface treatment materials of the positive electrodes in the same way as described in the first, second, and third preferred embodiments and carbon series composite materials which are different from the carbon plastics used in the first, second, and third preferred embodiments are used as the conductive electrode substrate materials indicated superior characteristic in the zinc-halogen secondary batteries. The following fourth and fifth preferred embodiments indicate superior characteristics of the zinc-halogen secondary batteries in which the other electrodes as described above were used.

FOURTH PREFERRED EMBODIMENT

The inventors selected three kinds of activated charcoal fibers from those shown in Table 1 and adhered them to glassy carbons GCR 101 (article number and manufactured by Kobe Seiko Kabushikikaisha) to discuss comparisons of electrode activites due to a difference in the electrode surface treatment materials.

The adhering method is such that a sheet of each of the activated charcoal fibers is laminated via a conductive carbon paste on the corresponding conductive electrode substrate and burned.

Then, three unit cells were prepared in which the electrode P comprising FE-400 and GCR 101, the electrode Q comprising KF-M-303 and GCR 101, and the electrode G comprising ACC 509-20 and GCR 101 were used as the respective positive electrodes and GCR 101 was used for each negative electrode, and RAI manufactured by Asahi Kasei Kabushikikaisha was used for each microporous sheet constituting the separation member. Each unit cell zinc-bromine secondary battery was charged for eight hours with the current density of 15 mA/cm^2 and was discharged with the same current density. Thereafter, the inventors compared and discussed each battery characteristic.

The result of each battery characteristic is shown in Table 3.

TABLE 3

		Performance of each battery (4), (5) and (6)			
Battery (No)	Kinds of positive and negative electrodes	Voltaic*1 Efficiency	Coulombic*2 Efficiency	Energy Efficiency	Remarks
Battery	Electrode	91.4%	90.5%	82.7%	15 A/cm^2

TABLE 3-continued

Battery (No)	Kinds of positive and negative electrodes	Performance of each battery (4), (5) and (6) Voltaic*1 Efficiency	Coulombic*2 Efficiency	Energy Efficiency	Remarks
(4)	(G) GCR 101				8 hour charge
Battery (5)	Electrode (P) GCR 101	82.1%	81.0%	66.5%	
Battery (6)	Electrode (Q) GCR 101	86.5%	82.8%	71.6%	

*1The discharge voltage at 0.5 volt cut off corresponds to an intermediate point of the discharge duration.
*2The discharge duration is an interval of time until 0.5 V cut off.

It is noted that the electrolyte used as 3 mol/l $ZnBr_2$ with which a bromine complexing agent is mixed and furthermore 4 mol/l NH_4Cl is added to improve conductivity. The electrolyte is recirculated as described before with reference to FIG. 1.

As appreciated from Table 3, the battery (4) in which the electrode G to which ACC 509-20 was adhered had superior characteristic in terms of each efficiency to the other batteries (5) and (6).

FIFTH PREFERRED EMBODIMENT

FIG. 5 shows a cross sectional view of a three-layer type electrode.

FIG. 6 shows a cross sectional view of a liquid static type unit cell of zinc-bromine secondary battery.

As shown in FIG. 5, the inventors selected three kinds of the activated charcoal fibers, i.e., FE-400, KF-M-303, and CC 509-20 shown in Table 1 as the activated charcoal fiber sheet **51** of the surface treatment materials. Each of these activated charcoal fiber sheet **51A** was brought in contact with PP-444 manufactured by Nikken Giken Kabushikikaisha as C/C composite **51B** (Carbon-Carbon composite) in the carbon series composite material. In addition, an ion exchange membrane **51C** was adhered to a surface of the C/C composite **51B** (PP-444) opposite to one of the activated charcoal fibers **51A** to form the three-layer type electrode **51**. It is noted that numeral **51D** denotes a mold resin. Such a three-layer type electrode **51** provides a holding effect of a halogen molecule Br_2 and so on. The inventors prepared the liquid static type unit cell of zinc-bromine secondary battery in which the above-described three-layer type electrode **51** was used as the positive electrode **5** and a zinc plate (a rolled zinc plate having a purity of 99.99%) was used as the negative electrode **6**, as shown in FIG. **6**. It is noted that, in FIG. **6**, numeral **61** denotes the electrolyte (3 mol/l $ZnBr_2+Br_2$), numeral **62** denotes an outer envelope made of a mold resin, numeral **52** denotes a lead terminal of the positive electrode **5**, numeral **64** denotes a lead terminal of the negative electrode **6**, and numeral **63** denotes an entrance of the electrolyte **61**.

The three kinds of batteries (7), (8) and (9) prepared in the way described above were charged for one hour with the current density of 15 mA/cm^2 and discharged with the same current density.

Table 4 and FIG. 7 show each battery characteristic of the three kinds of batteries (7), (8), and (9). It should be noted that the discharge voltage was zero volt when the discharge operation is ended.

As shown in Table 4 and FIG. 7, the battery (7) in which ACC 509-20 is used as a surface treatment material has a longer duration time than the other two kinds of batteries (8) and (9) and operates with superior values of the charge and discharge voltages to those of the other batteries (8) and (9).

TABLE 4

Characteristics of Batteries (7), (8) and (9) Battery No.	Battery (7)	Battery (8)	Battery (9)
Kinds of Activated Charcoal Fibers Used in Positive Electrode	ACC509-20	Fineguard FE-400	KF-M-303
Voltage (V) at Initial Stage of Charge	2.1	2.2	2.1
Voltage (V) at Final Stage of Charge	2.2	2.4	2.3
Voltage (V) at Initial Stage of Discharge	1.9	1.5	1.7
Discharge*1 Duration (min)	57	48	50
Coulombic*2 Efficiency (%)	95	80	83
Remarks	Good Moldability	Carbon Powders was Generated During the Molding Operation	Carbon Powders was Generated During the Molding Operation

*1The discharge was cut off at zero volt. The discharge duration was an interval of time until zero volt was reached.
*2Coulombic efficiency = quantity of discharge electricity/quantity of charge electricity

As the result of fourth and fifth preferred embodiments, the activated charcoal fiber ACC 509-20 of the novoloid type of the phenol resin series indicated a superior characteristic in the activity when any arbitrary electrode substrate material was used. Especially, the activated charcoal fiber ACC 509-20 indicated a superior electrochemical reactivity to the other activated charcoal fibers due to the large relative surface area that it has. Consequently, the inventors admitted that it was reasonable for the activated charcoal fiber ACC 509-20 to be used as the surface treatment material of the positive electrode in the zinc-halogen secondary battery.

EFFECT

Since the phenol resin series activated charcoal fiber sheets have large relative surface areas, large adsorption quantities, and pores whose diameters have distribution peaks from 1.5 nm to 3.5 nm, they indicate good electrochemical reactions for active materials in the electrolytes. In addition, since the above-described activated charcoal fiber sheets have large percentage elongations and small modulus of elasticity, they are flexible and have good workabilities.

As described above, since the phenol resin series activated charcoal fibers have higher tensile strength and tensile modulus than the rayon and acryl series carbon fiber sheet, they can only withstand mechanical pressure and heat under which surface treatment materials of electrodes used in zinc-halogen secondary batteries are adhered to the electrode substrate material but also achieve better battery characteristics due to remarkably larger surface areas of the carbon fiber sheets themselves.

Table 5 shows general characteristics of each typical activated charocal fiber sheet.

TABLE 5

characteristics	Phenol Resin Series	Rayon Series	Acryl Series	Granulated Carbon
Fiber diameter (μm)	9 to 11	15 to 20	6 to 8	—
Relative Surface Area (m^2/g)	1500 to 2000	1400	900	800
Pore Diameter (nm)	1.5 to 3.5	114	1.0	1.5 to 2.5
Tensile Strength (kg/mm^2)	30 to 40	5 to 10	30	—
Tensile Modulus (kg/mm^2)	1000 to 1500	—	7000 to 8000	—

SI unit: kg/mm^2 = 9.807 MPa

The above-described surface treatment electrodes in which one of the phenol resin series activated charcoal carbon fiber sheet having its weight per unit area equal to or more than 100 g/m^2, pore diameters whose distribution peaks are 1.5 to 3.5 nm and whole relative surface area equal to or more than 1500 m^2/g are used as the positive electrode surface treatment materials according to the present invention has the following superior characteristics than the surface treated electrodes as the treatment materials of which activated charcoal fiber sheets belonging to any one of rayon series, cellulose series, and acryl series are used.

(1) Since the phenol resin series activated charcoal fibers manufactured by Nihon Kynol Company Limited as described above have larger halogen (bromine) holding capacities than the cellulose series, rayon series, and acryl series activated charcoal fibers, the actual characteristics thereof when they are adhered to the conductive electrode substrates are remarkably improved and especially the discharge characteristics required for the secondary batteries were remarkably improved.

(2) Since the activated charcoal fibers manufactured by Nihon Kynol Company Limited have high mechanical strength, i.e., high tensile strength and low tensile modulus in their fibers themselves, the fibers are seldom destroyed during the adhering process under mechanical pressure and heat to the conductive electrode substrate. Consequently, the carbon plastic electrode having a large relative surface area and to which such an activated charcoal fiber is adhered under mechanical pressure and heat in a metallic die can properly be manufactured.

Furthermore, the electrodes in which the activated charcoal fibers whose originating raw materials are the phenol resin series novoloid fibers are adhered to the glassy carbons in a conventional method can achieve superior characteristics than those in which the activated charcoal fibers of the other PAN series or rayon series are adhered to the conductive electrode substrates. In addition, the electrodes having the three-layer constructions using the activated charcoal fibers whose originating raw materials are the penol resin series novoloid fibers, C/C composites, and ion exchange fibers exhibit proper electrode characteristics such that discharge durations are longer than those manufactured using the PAN series or rayon series activated charcoal fibers.

It will clearly be understood by those skilled in the art that the foregoing description is made in terms of preferred embodiments and various changes and modifications are made without departing from the scope of the present invention which is to be defined by the appended claims.

What is claimed is:

1. A surface treated electrode for a zinc-halogen secondary battery, comprising:
(a) an electrically conductive material made of a carbon plastic formed in a sheet shape with a conductive carbon powder and thermoplastic constituting a substrate of the electrode; and
(b) a surface treatment material integrally formed on the conductive electrode substrate material under a heat and pressure adhesion, the surface treatment material satisfying predetermined characteristics such that a weight per unit area thereof is at least about 100 g/m^2, pore diameter distribution peak is about from 1.5 nm to 3.5 nm, a surface area of a part occupied by pores whose diameters are about from 1 nm to 11 nm is at least about 30 m^2/g, a tensile strength is at least about 294 MPa, and a tensile modulus is up to about 14710.5 MPa.

2. The surface treated electrode as set forth in claim 1 wherein the surface treatment material is made of a phenol resin series activated charcoal fiber.

3. The surface treated electrode as set forth in claim 1, wherein said conductive electrode substrate material is a glassy carbon.

4. The surface treated electrode as set forth in claim 1, wherein said conductive substrate material is a carbon plastic.

5. The surface treated electrode as set forth in claim 1, wherein said conductive substrate material comprises a Carbon-Carbon composite material, to one surface of which the surface treatment material is adhered and to the opposite surface of which an ion exchange fiber is adhered.

6. The surface treated electrode as set forth in claim 4, wherein the phenol resin series activated charcoal fiber is adhered onto the carbon plastic material under mechanical pressure and heat.

7. The surface treated electrode as set forth in claim 4, wherein the phenol resin series activated charcoal fiber is attached onto the carbon plastic material surface.

8. The surface treated electrode as set forth in claim 1, wherein the surface treated electrode is a positive electrode of a zinc-halogen secondary battery.

9. The surface treated electrode as set forth in claim 8, wherein the surface treated electrode is a positive electrode of a zinc-bromine secondary battery.

10. A surface treated electrode for a positive electrode of a zinc-halogen secondary battery, comprising:
(a) an electrically conductive material made of a carbon plastic formed in a sheet shape with a conductive carbon powder and thermoplastic constituting a substrate of the positive electrode; and
(b) a surface treatment material integrally formed on the conductive substrate material under a heat and pressure adhesion, the surface treatment material having predetermined characteristics such that a weight per unit area thereof is at least about 100 g/m^2, pore diameter distribution peak is about from 1.5 nm to 3.5 nm, a surface area of a part occupied by pores whose diameters are about from 1 nm to 11 nm is at least about 30 m^2/g, a tensile strength is at least about 294 MPa, and a tensile modulus is up to about 14710.5 MPa.

11. The surface treated electrode as set forth in claim 10, wherein the electrically conductive material comprises a carbon plastic which has a weight ratio of polyethylene to carbon black of about 100:50 and onto which the surface treatment material is adhered under predetermined mechanical pressure and heat.

12. The surface treated carbon plastic electrode as set forth in claim 10, wherein the electrically conductive electrode substrate material comprises a carbon plastic which has a weight ratio of polyethylene, carbon black, and graphite of about 50:15:35 and onto which the surface treatment material is adhered under a predetermined mechanical pressure and predetermined temperature using a predetermined die for a predetermined interval of time.

13. The surface treated electrode as set forth in claim 12, wherein the predetermined pressure is about 5.88 MPa, the predetermined temperature is about 140° C., and the predetermined interval of time is about three minutes.

14. The surface treated electrode as set forth in claim 12, wherein the surface treatment material is the phenol resin series activated charcoal fiber derived from an activation and sintering of a novoloid of phenol formaldehyde under vaporized water after a melt spinning of the novoloid.

15. The surface treated carbon plastic electrode as set forth in claim 12, wherein the surface treatment material is cloth and has a weight per unit area in a unit of sheet of about 135 g/m^2, a thickness of about 0.53 mm, relative surface area of about 1500 m^2/g, pore diameter of about from 1.5 nm to 3.5 nm.

16. The surface treated electrode as set forth in claim 15, wherein the carbon plastic electrode substrate material has a thickness of about 1.50 mm, a resistivity of about 0.168 Ω-cm, a relative surface area of about 995 m^2/g, and a tensile strength of about 3129.205 MPa.

17. The surface treated electrode as set forth in claim 10, wherein the positive electrode surface treatment material is the phenol resin series activated charcoal fiber having a weight per unit area in a unit of sheet of about 100 g/m^2, a thickness of about 2.20 mm, a relative surface area of about 2000 m^2/g, pore diameters ranging from about 1.5 nm to 3.5 nm and a felt form.

18. The surface treated electrode for a positive electrode of a zinc-halogen secondary battery as set forth in claim 17, wherein the zinc-halogen secondary battery includes: the positive electrode constituted by the conductive electrode substrate material comprising the carbon plastic having a weight ratio of polyethylene to carbon black of about 100:50 and onto the surface of which the positive electrode surface treatment material is adhered under mechanical pressure and heat; a negative electrode formed of zinc plate; and an electrolyte of $ZnBr_2$ having a concentration of about 3 mol/l and the zinc-halogen secondary battery has an interelectrode distance of 10 mm without an electrode separating member and wherein the zinc-halogen secondary battery including the phenol resin series activated charcoal fiber of the surface treatment material has a higher discharge voltage and longer discharge duration than the zinc-halogen secondary battery including the phenol resin series activated charcoal fiber of the positive electrode surface treatment material, said positive electrode surface material comprising cloth having a weight per unit area in a unit of sheet of about 115 g/m^2, a thickness of about 0.44 mm, a relative surface area of about 2000 m^2/g, pore diameters ranging from 1.5 nm to 3.55 nm when both zinc-halogen secondary batteries are charged for one hour at current densities of 20 mA/cm^2 and discharged with the same electrolytes renewed.

19. The surface treated electrode as set forth in claim 10, wherein the conductive electrode substrate material comprises a glassy carbon onto which a sheet of the activated charcoal fiber phenol resin series having a predetermined characteristic such that a weight per unit area is 170 g/m^2, a thickness is 0.60 mm, a relative surface area is 2000 m^2/g, a pore diameter ranges from 1.5 nm to 3.5 nm, and fiber form is of a cloth form is laminated via a condutive carbon paste.

20. The surface treated electrode as set forth in claim 10, wherein the conductive electrode substrate material comprises a Carbon-Carbon composite material, to one surface of which the phenol resin series activated charcoal fiber is adhered as the surface treatment material and to the opposite surface of which an ion exchange fiber is adhered and which further comprises a rolled zinc plate as a negative electrode having a purity of 99.99% and an electrolyte of 3 mol/l $ZnBr_2+Br_2$.

* * * * *

US005595659A

United States Patent [19]

Huang et al.

[11] Patent Number: 5,595,659

[45] Date of Patent: Jan. 21, 1997

[54] FILTER MATERIAL FOR REMOVING CHLORINE FROM COLD WATER IN PREPARING A HUMAN-CONSUMABLE BEVERAGE

[75] Inventors: **Ming-Teh Huang**, Durham; **David R. Lambert**, Somersworth; **Robert F. Gatta**, Durham; **Kevin G. Lynch**, Hampton, all of N.H.

[73] Assignee: **Lydall, Inc.**, Manchester, Conn.

[21] Appl. No.: **390,672**

[22] Filed: **Feb. 17, 1995**

[51] **Int. Cl.**[6] **B01D 39/02**

[52] **U.S. Cl.** **210/502.1**; 210/504; 210/505

[58] **Field of Search** 210/503, 504, 210/505, 506, 507, 508, 502.1

[56] **References Cited**

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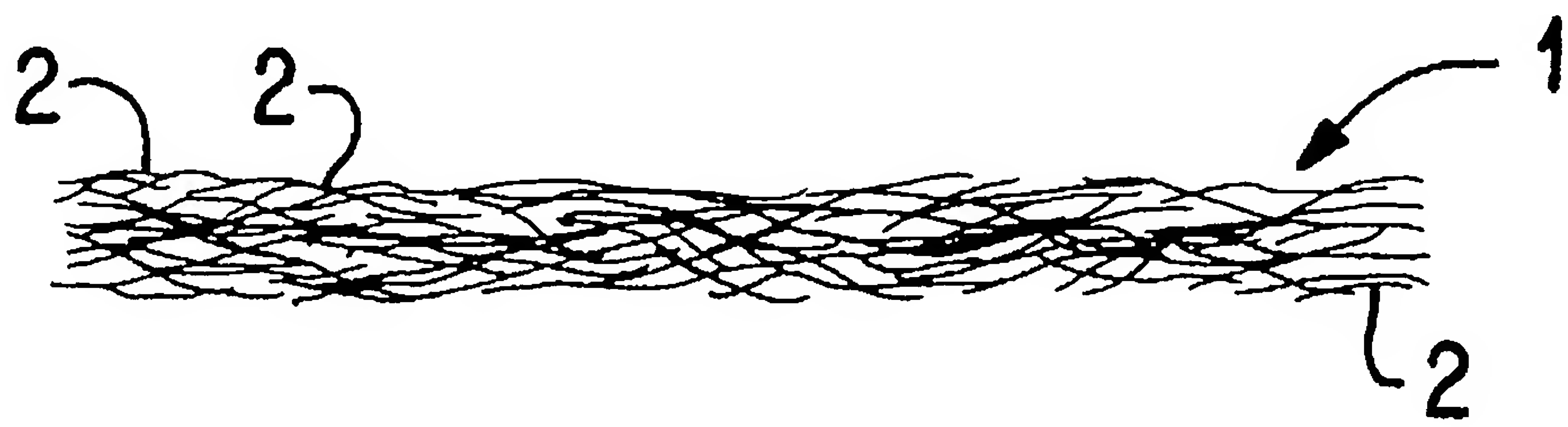
Primary Examiner—Frank Spear

Attorney, Agent, or Firm—Griffin, Butler, Whisenhunt & Kurtossy

[57] **ABSTRACT**

A filter material for removing chlorine from cold water used in preparing a human-consumable beverage having at least one layer of a mat of laid fibers of cellulosic fibers and synthetic textile fibers and mixtures thereof. A synthetic hydrophilic, food-grade latex binder deposited onto the fibers within the mat in an amount sufficient to so bind the fibers together within the mat that during a filtration of cold water through the mat no substantial amount of fibers are displaced therefrom and in an amount insufficient to substantially reduce a gravity flow rate of cold water through the mat to less than about 0.3 liter per minute per 100 square centimeters of the mat. A water-insoluble chlorine adsorbent or absorbent solid powder disposed on the binder such that no more than 65% of the total outside surface area of the powder is substantially contacted by the binder.

37 Claims, 3 Drawing Sheets



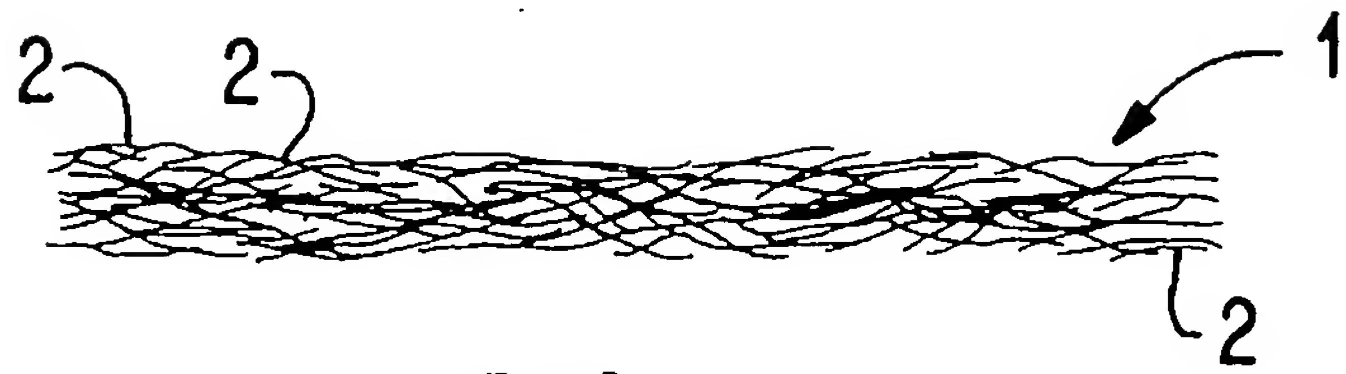


FIG. 1

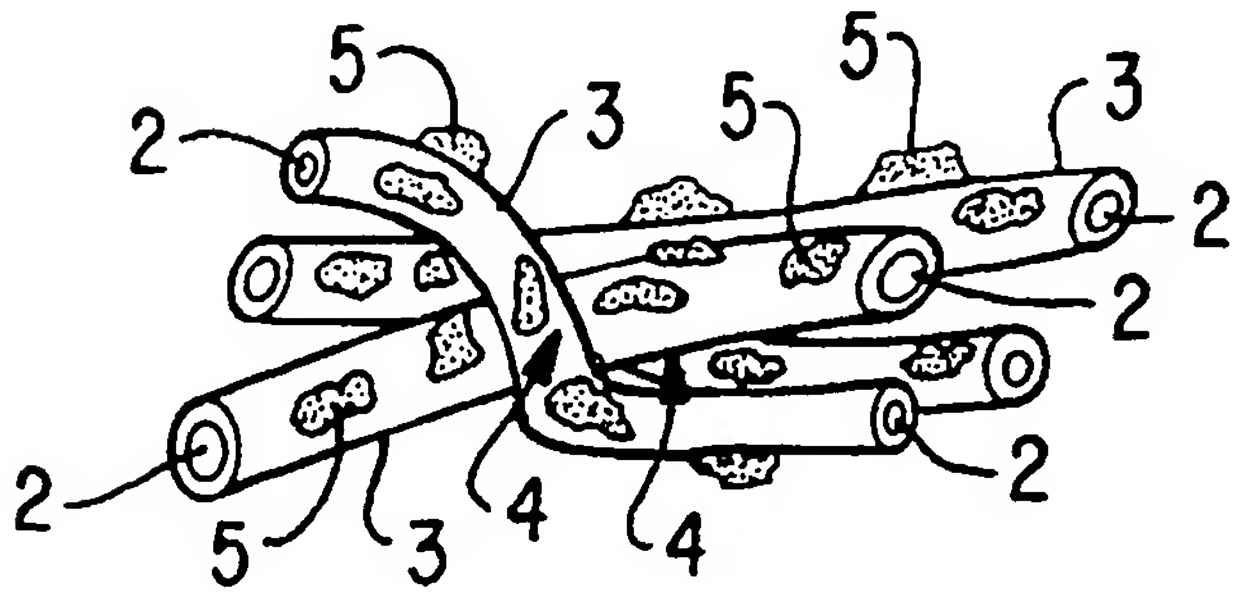


FIG. 2

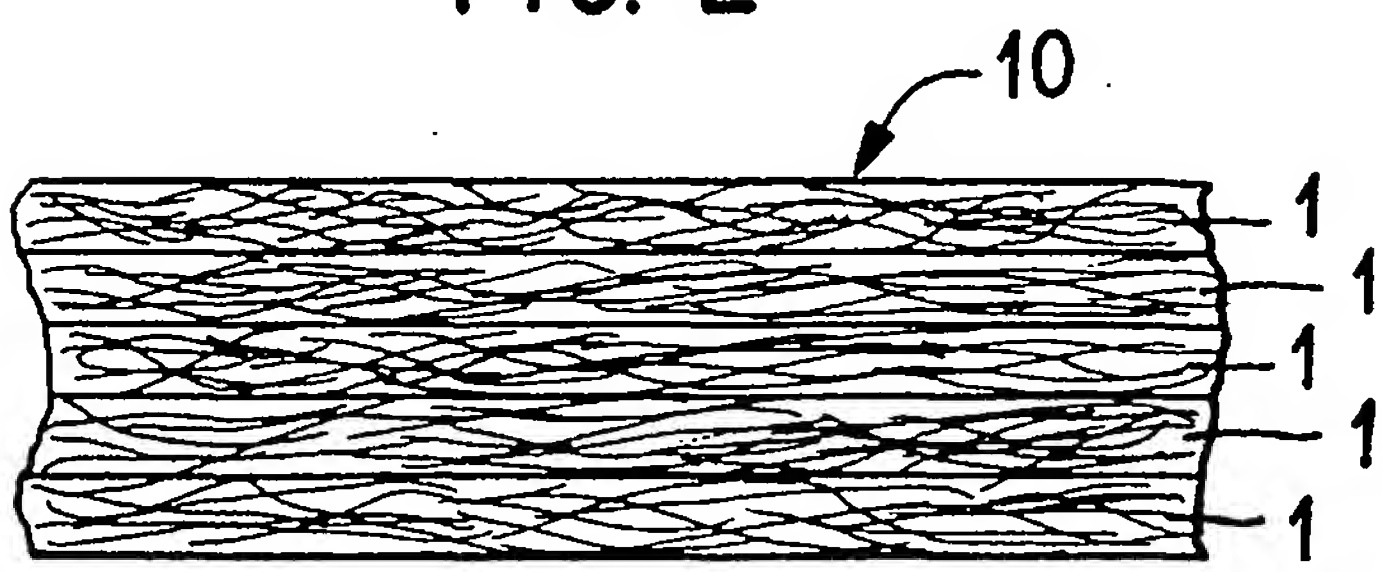


FIG. 3

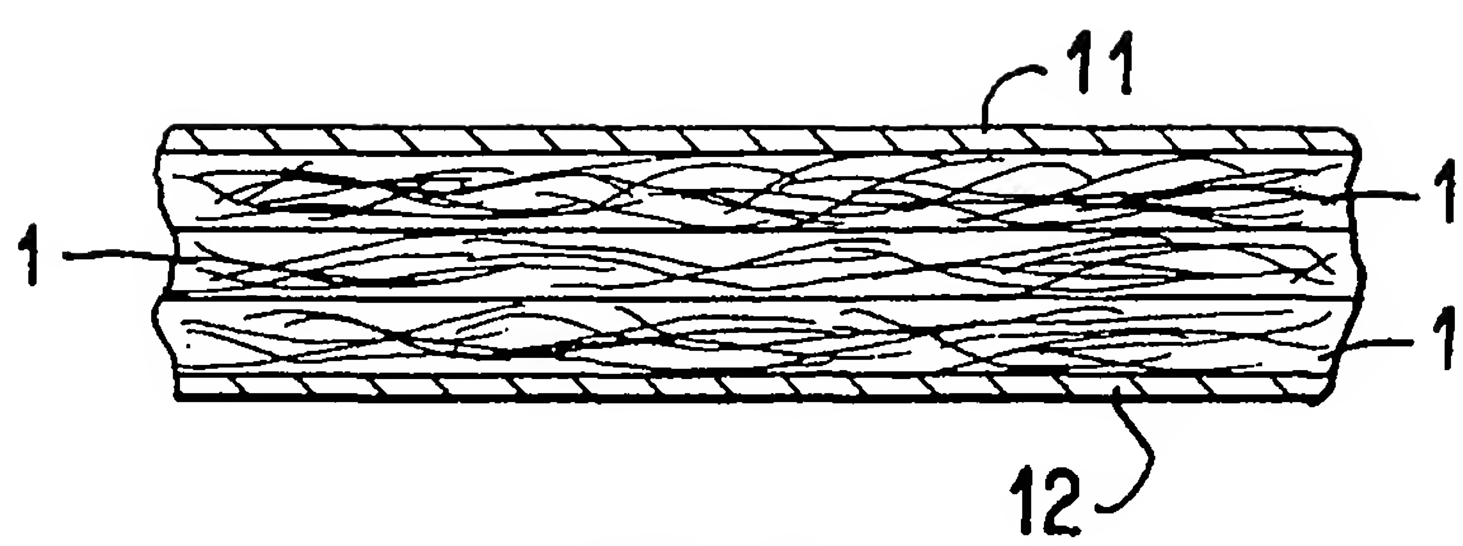


FIG. 4

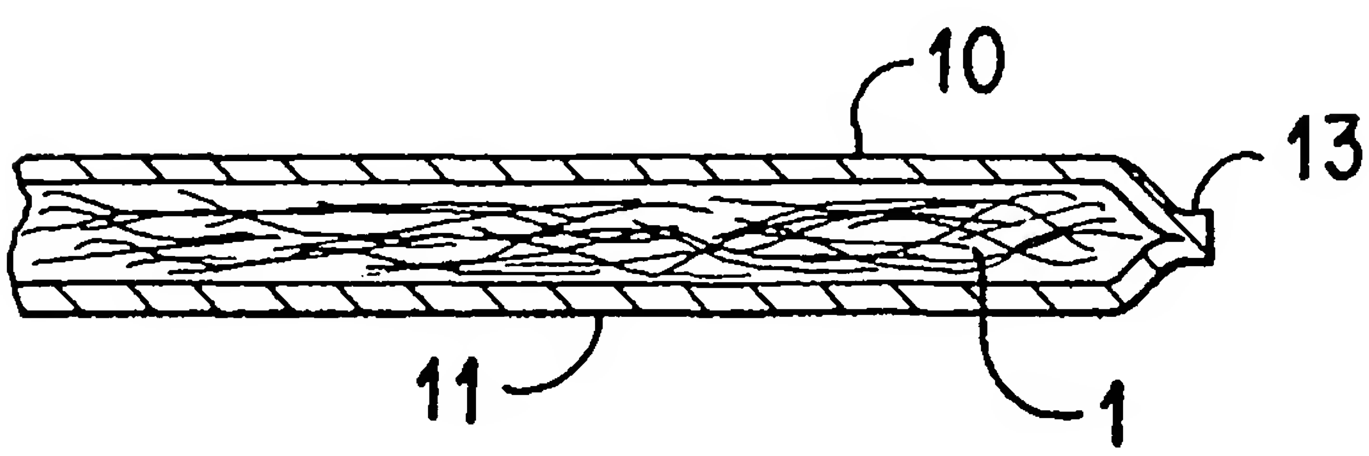


FIG. 5

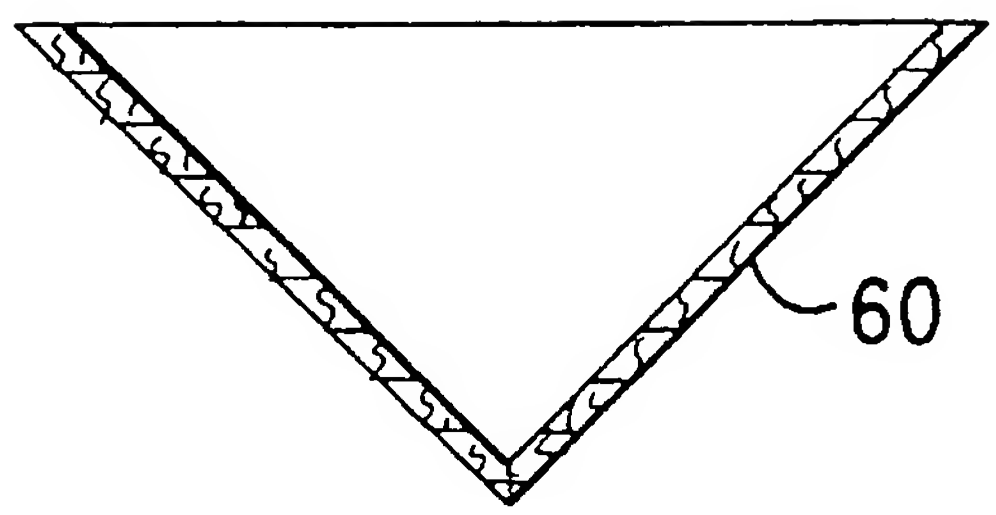


FIG. 6

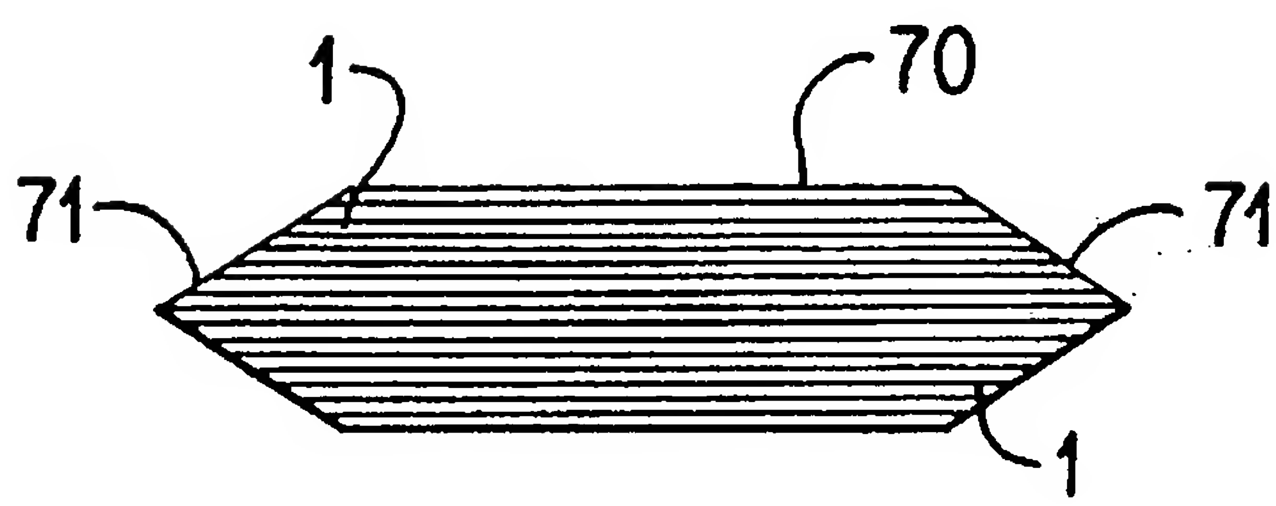


FIG. 7

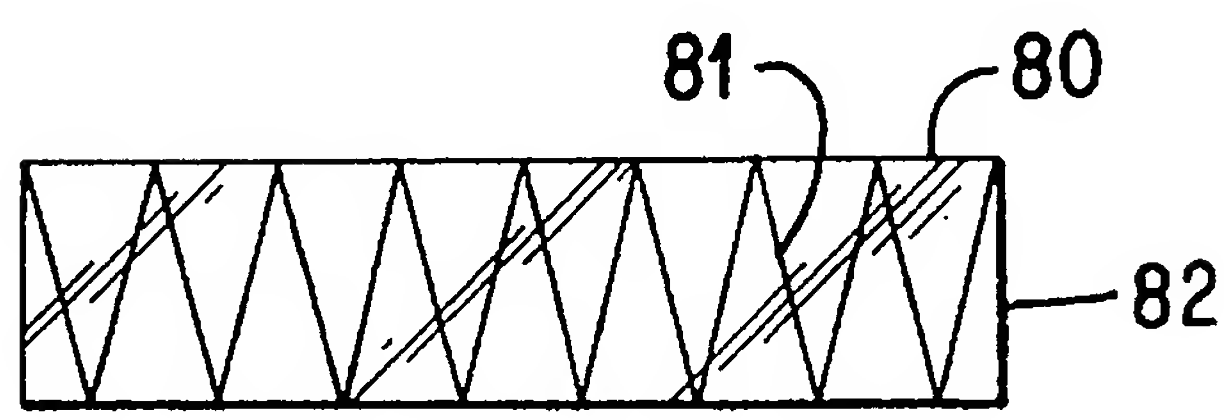


FIG. 8

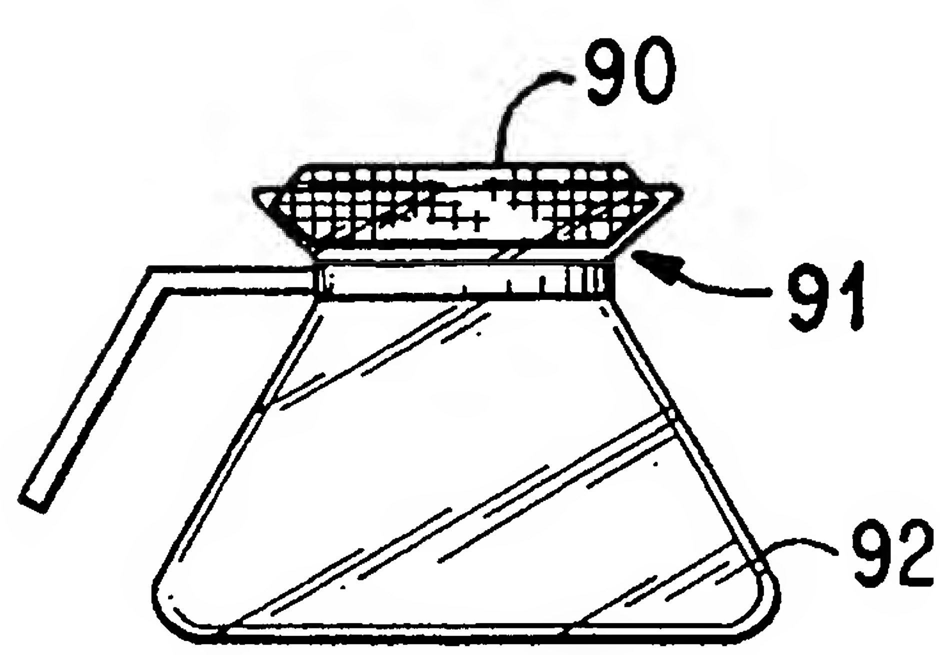


FIG. 9

FIG. 10

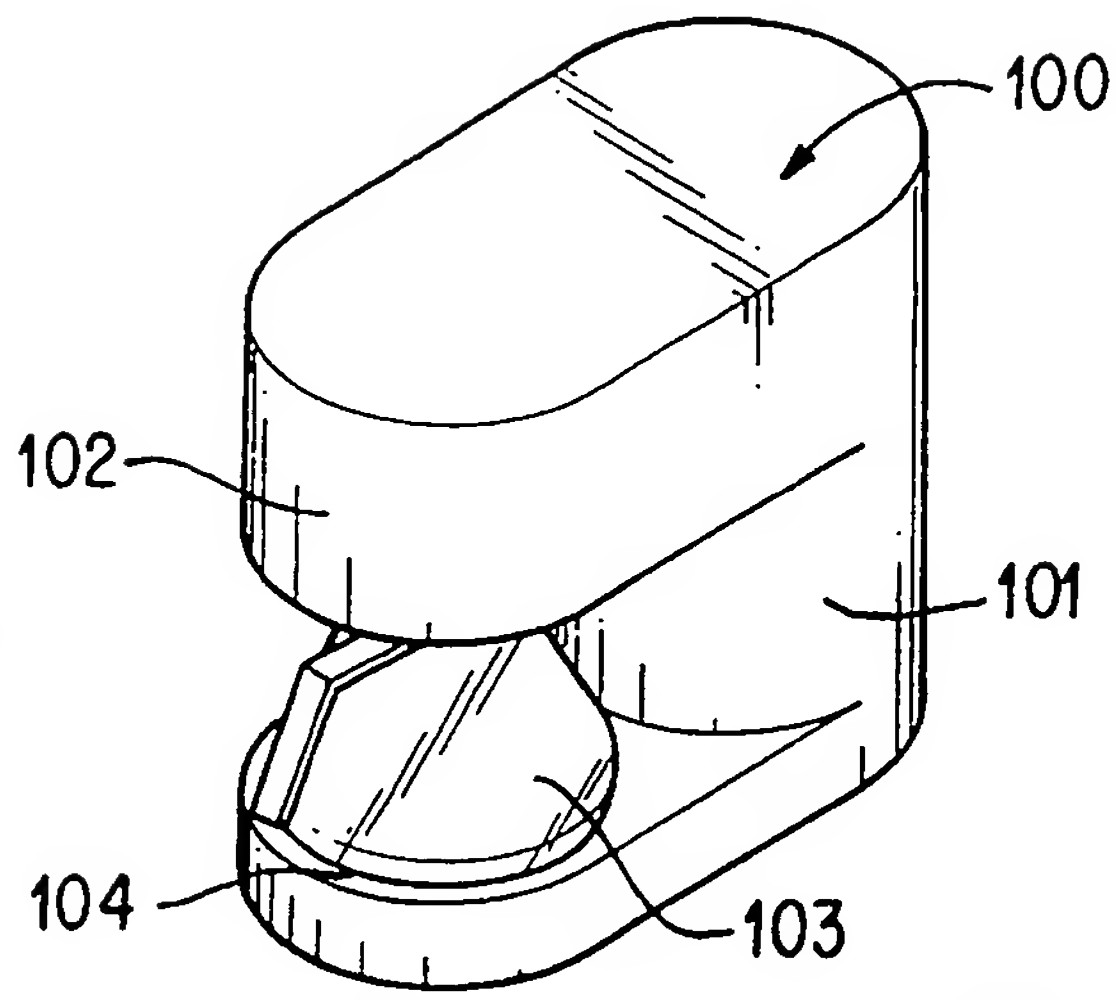


FIG. 11

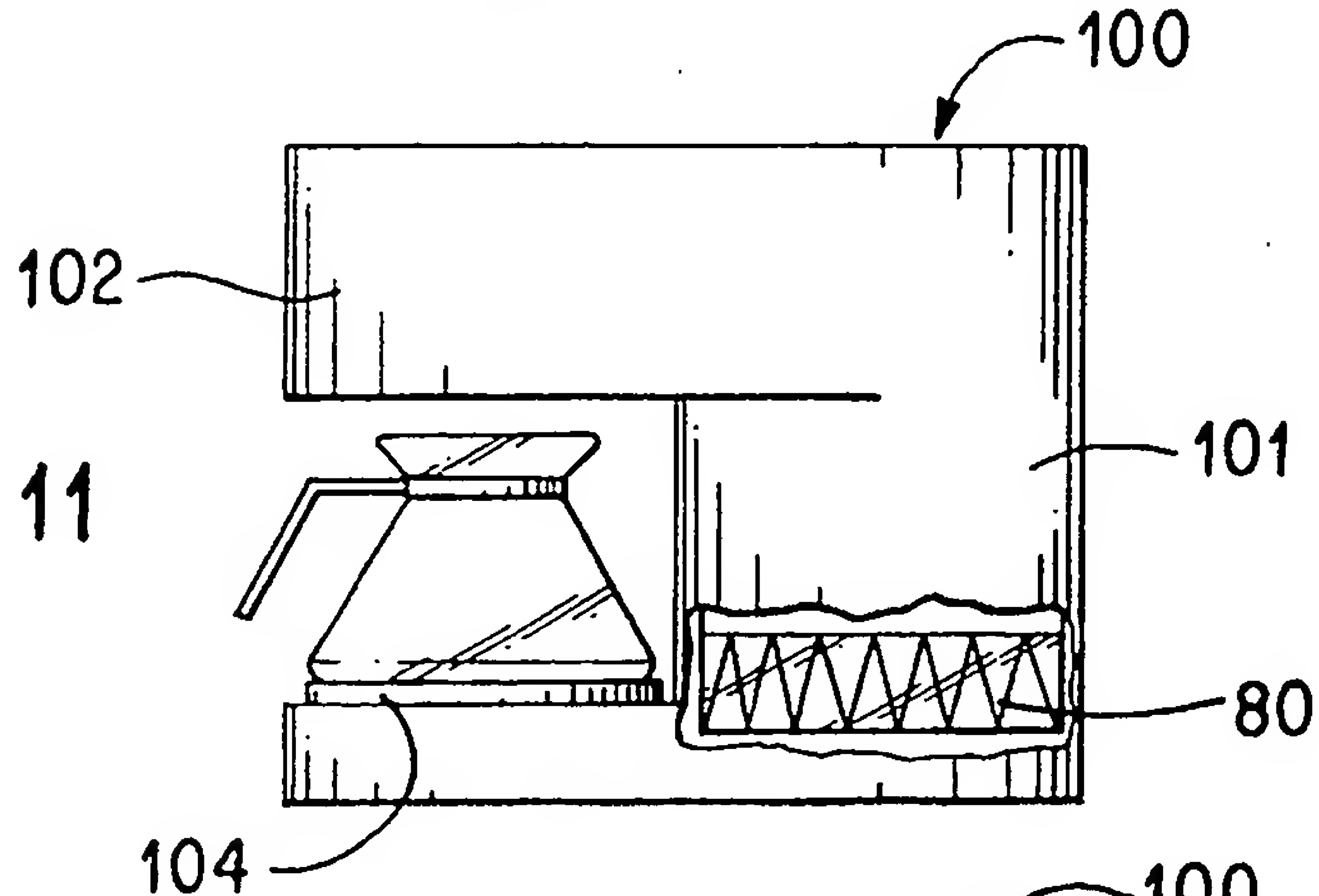


FIG. 12

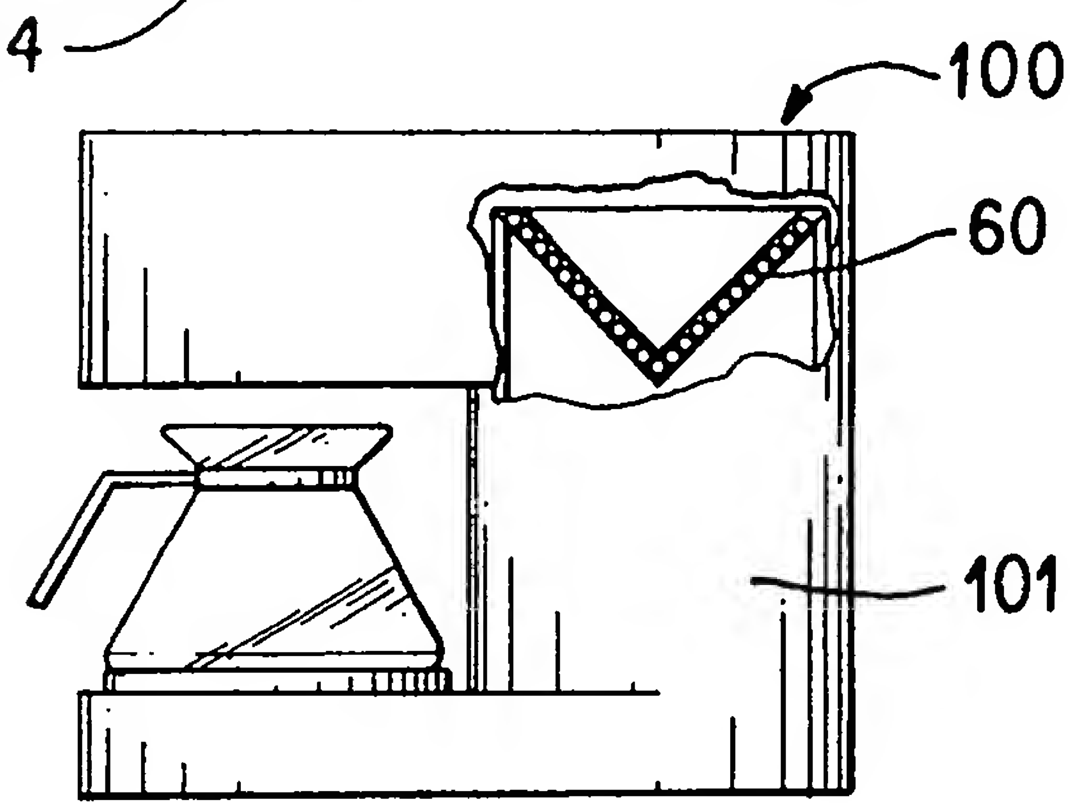
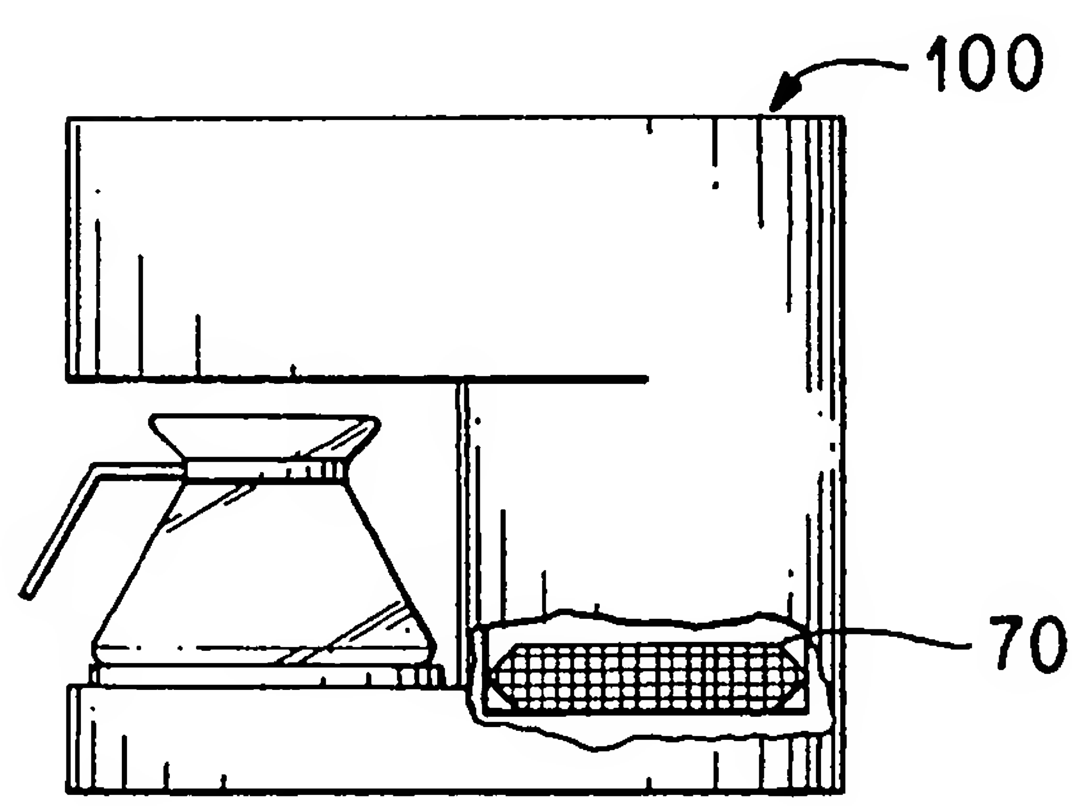


FIG. 13



FILTER MATERIAL FOR REMOVING CHLORINE FROM COLD WATER IN PREPARING A HUMAN-CONSUMABLE BEVERAGE

The present invention relates to a filter material which is capable of removing chlorine from water such that the water is more acceptable for use in preparing human-consumable beverages, especially in that the taste of the water and, hence, the taste of the beverage is improved.

BACKGROUND OF THE INVENTION

It has long been known that typical city water supplies have a variety of contaminants which contribute to an unpleasant taste of a beverage made from that city water. Among these contaminants are lead, hydrocarbons, calcium, iron, sulfides, and especially chlorine used in purifying the city water. While all of these contaminants contribute to the unpleasant taste of beverages prepared from such city water, chlorine is probably the most usual and troublesome contaminant, since it is normally present in all city water, due to the purification process, and since it can be detected in beverages in very small amounts. While the unpleasant taste of the beverage prepared from such city water is detectable in almost every beverage so prepared, including reconstituted orange juice, soft drinks, iced drinking water, and the like, it is particularly troublesome in connection with beverages which are heated during preparation, e.g. tea and coffee.

The art has long sought effective means of removing such contaminants, especially chlorine, from such city water, and a number of approaches in the art have been taken. For example, one approach is that of a porous plastic film filter with pores sufficiently small to filter contaminants, such as chlorine, from the water, but such filters have a very low gravity flow rate, and to use such filters requires considerable time for filtration of the water in beverage preparation.

Another approach is that of providing a matrix of fibers and activated charcoal where the activated charcoal will remove contaminants, especially chlorine, but to make such filters satisfactory, the fibers must be made of materials which will not support bacterial growth, since, otherwise, continued use of such filters would cause a health problem. To substantially avoid bacterial growth, such filters, with activated carbon therein, are made with hydrophobic synthetic polymer fibers, which are generally non-porous, and hence will not support bacterial growth resulting from absorbed nutrients from the water. However, filters made from such hydrophobic fibers have a very low gravity flow rate, and to be useful in a practical sense, filters of that nature must be operated under substantial pressure, e.g. city water pressure. Thus, filters of that nature have been limited, generally, to "in-line" filters, i.e. filters disposed in the city water pressure lines of a house, manufacturing facility, or the like or at the taps thereof. These filters, therefore, operate generally with city water pressure, e.g. about 40 psi or more. While this arrangement is satisfactory for in-line filters, such an arrangement is not satisfactory for gravity flow filters. In addition, filters of this nature must be contained in a canister and protected by media around the filter for preventing particles of activated carbon from passing through the filter, during use, and into the consumable water. This further decreases the pressure drop across those filters and, consequently, requires the higher city water pressures for effective use thereof.

Efforts have been made in the art to improve flow rates with less pressure for effective use thereof, and U.S. Pat. Nos. 4,395,332; 4,505,823; and 4,569,756 are representative thereof. These patents describe filters for removing contaminants from water, where the filters contain cellulose fibers and an additional strengthening fiber, such as a polyester fiber, as well as a contaminant adsorbent, which, among others, can be activated carbon or charcoal. In addition, these filters contain micro-bits of polymers, which polymers can be, for example, polystyrene polymers, polyolefin polymers and the like. These micro-bits retain porosity in the filters and, therefore, provide greater flow rate with less pressure drop through the filters. Thus, the filters are said to be useful for filtering tap water for drinking and cooking use in a gravity flow filter device and, particularly, a conical filter for filtering tap water from a tap with such conical filter device is disclosed. However, the filters of these patents, while said to be useful in filtering tap water by gravity flow filtration for drinking and cooking purposes, are composed, in a specific example, of cellulose fibers, polyester fibers, activated charcoal, a binder for binding the fibers together to improve the strength thereof, and the micro-bits, which combination still has a very low gravity flow filtration rate. While that low filtration rate is suitable for some purposes, it is not suitable for a variety of other purposes.

In this latter regard, as noted above, beverages which are heated in preparing the beverage are particularly susceptible to the taste of tap water contaminants, especially chlorine, and very typical of such beverages are coffee and tea. Both coffee and tea may be brewed in a conventional coffee making machine, where cold water is heated by an electrical heating element and, after being heated, is fed through a basket containing the coffee or tea by which the brewed coffee or brewed tea is made and discharged from that basket by gravity into a pot. As the art has well appreciated, in order to make a filter suitable for such machines, the filter must have a flow rate consistent with the brewing rate of the machine. Otherwise, the time for brewing, for example, a pot of coffee, would be greatly increased, and the heating element of the machine could be starved for water and burn out or the hot water supplied to the basket containing the tea or coffee could be seriously reduced, and ineffective brewing and long brewing time would result. Thus, gravity filters with such reduced flow rates are not satisfactory for those purposes. Moreover, those patents do not describe any practical means of retaining the activated charcoal in the filter, and any substantial amount of activated charcoal that passes through the filter into the brewed coffee or tea, of course, would be quite unacceptable.

A somewhat similar but yet slightly different approach in the art is described in U.S. Pat. No. 4,160,059, where a filter is proposed that is made of wood pulp and/or synthetic fiber, a heat-fusible fiber, and an adsorptive material, such as activated charcoal. The heat-fusible fiber is heated to fuse the charcoal to the fibers of the filter, which, therefore, presumably locks the activated charcoal particles in place and prevents that activated charcoal from passing through the filter and into a beverage. This fusing of the charcoal particles to the fibers is considered a better approach than that of the prior art where latex binders have been used for binding the charcoal to fibers.

In this latter regard, U.S. Pat. No. 3,158,532 teaches a filter material made of various fibers, including polyester fibers and paper fibers, and a bonding agent or binder for binding particulate material to deposited layers of fibers, and the particulate material, in addition to a number of others, can be activated carbon. Among the binders suggested are polyacrylic resins.

It has also long been recognized that hydrophilic fibers forming a filter material will substantially increase the flow rate of water and similar water-containing fluids through the filter, and commercial milk filters are commonly made of cellulose fibers for this purpose, e.g. cotton, rayon and mixtures thereof. Such filters have also been made with a combination of rayon fibers and synthetic fibers, such as polyester fibers, polyolefin fibers, polyacrylate fibers, and polyamide fibers, in order to provide better physical properties to those filters, and U.S. Pat. No. 3,307,706, is representative thereof.

Various forms of filters using activated carbon have also been described in the art, such as pleated forms and tape-like porous material, and U.S. Pat. Nos. 4,130,487 and 4,645,597 are representative thereof.

From the foregoing, it can be seen that the art has approached filters of the present nature from various directions, but the art has not been successful in providing a filter which will give high flow rates of gravity-filtered water, which will remove substantial amounts of contaminants, especially chlorine, which will ensure that a chlorine absorbent or adsorbent will not be displaced from the filter and into the water for producing the beverage, which will not support bacterial growth with considerable reusage of the filter, and which can be so inexpensively produced as to be practical, especially, for home use, and more especially in conventional coffee making machines. It would, therefore, be of considerable advantage to the art to provide a filter which meets all of the foregoing requirements, and which, in addition, can remove very substantial amounts of contaminants, especially chlorine.

BRIEF DESCRIPTION OF THE INVENTION

The present invention, therefore, provides a filter material for removing chlorine (as well as other contaminants) from cold water used in preparing a human-consumable beverage and which can be reused a number of times with safety and which will provide a high flow rate with gravity filtration. The invention is based on several primary and several subsidiary discoveries.

First of all, it was discovered that the dilemma of the art of hydrophilic fibers versus hydrophobic fibers briefly mentioned above can be solved. Thus, while hydrophilic fibers, such as cellulose fibers, provide much higher gravity flow rates, those fibers, being pervious to water, can support bacterial growth on absorbed nutrients from the water and are therefore not acceptable for serial, time spaced-apart uses of the filter. On the other hand, synthetic hydrophobic fibers, such as polyester fibers, are not pervious to water and, hence, will not support bacterial growth, due to the lack of absorbed nutrients from the water for bacterial growth, but those fibers, being hydrophobic, seriously decrease the gravity flow rate of a filter made therefrom. This dilemma of the art has been solved by the present invention in that either or both of cellulosic fibers or synthetic fibers may be used to provide an effective filter with high gravity flow rates when those fibers have deposited thereon a food-grade hydrophilic latex binder. With such binder substantially coating the fibers of the filter, the filter will have high gravity flow rates because of the hydrophilic nature of the binder, irrespective of whether the fibers are hydrophobic, e.g. polyester fibers, or hydrophilic, e.g. cellulosic fibers. In addition, since the binder is a food-grade binder, it will not, by definition, support bacterial growth, even when used for a number of serially, time spaced-apart filtrations.

As a subsidiary discovery in this regard, it was found that acrylic latex binders are particularly useful in this regard, since those binders provide more of a sticky property for adhering activated charcoal to the binder, as described below.

As a further primary discovery, it was found that the amount of the binder deposited onto the fibers within a mat of fibers must be sufficient to so bind the fibers together within the mat that, during filtration of cold water through the mat, no substantial amount of fibers are displaced from the mat but, at the same time, in an amount insufficient to substantially reduce a gravity flow rate of cold water through the mat to less that 0.3 liters per minute per 100 square centimeters of the mat.

Thus, by providing, substantially a covering of the hydrophilic food-grade latex binder on the fibers, bacterial growth will be inhibited, even with serial, time spaced-apart uses of the filter, while, at the same time, the gravity flow rate through the filter will be maintained at a rate sufficient for use in conventional devices, such as coffee making machines.

A third primary discovery again solves a dilemma in the art. While the art, as noted above, had used binders in connection with such filters, activated charcoal, in the form of a powder, was substantially "blinded" by the binders, i.e. the binders substantially covered the particles of activated charcoal and "blinded" those particles from removing contaminants, especially chlorine. On the other hand, if such binders were not used, or used in such small amounts so as to avoid that blinding of the activated charcoal, the activated charcoal was liable to pass through the filter and into the water used for making beverages, which is quite undesirable. This dilemma in the art was solved by an arrangement such that the powder used for adsorbing or absorbing contaminants, e.g. chlorine, such as activated charcoal, is disposed on the binder, as opposed to largely within the binder, and disposed on the binder such that no more than 65% of the total outside surface area of the powder is substantially contacted by the binder, and preferably a much smaller percentage thereof. This still provides considerable outside surface area of the powder for removing contaminants. At the same time, that powder is so attached to the binder that it will not be displaced during use of the filter and into the water intended for beverage making.

As a subsidiary discovery, it was found that the stickiness of the binder may be such as to provide good adhesion of fibers to fibers such that the mat forming the filter material has high strengths and can be manipulated and used a number of times without being substantially disrupted or the fibers displaced from the filter into the water or so displaced that channeling or the like of the water through the filter occurs, which is, of course, not desired.

As another primary discovery, it was found that the powder could be deposited onto the binder, in the above-described manner, by a step in a process for making the filter material. In this regard, an emulsion-breaking agent is added during processing of the fibers and binder such that the latex binder, in emulsion form, precipitates onto the fibers, and, thereafter, the powder is added to that combination such that a large portion of the surface area of the powder remains out of contact with the binder, while at the same time the powder is firmly attached to the binder and will not be displaced.

Thus, briefly stated, the present invention provides a filter material for removing chlorine from cold water used in preparing a human-consumable beverage. The filter material comprises at least one layer of a mat of laid fibers selected

from the group consisting of cellulosic fibers and synthetic textile fibers and mixtures thereof. A synthetic hydrophilic food-grade latex binder is deposited onto the fibers within the mat in an amount sufficient to so bind the fibers together within the mat that, during a filtration of cold water through the mat, no substantial amount of fibers are displaced therefrom and in an amount insufficient to substantially reduce a gravity flow rate of cold water through the mat to less than 0.3 liters per minute per 100 square centimeters of the mat. A water-insoluble chlorine adsorbent or absorbent solid powder is disposed on the binder such that no more than 65% of the total surface area of the powder is substantially contacted by the binder.

In the method of the invention, the fibers are mixed in water to form a dispersion of the fibers in the water. The latex binder in the form of an emulsion is added and mixed with the dispersion to form a dispersed mixture of the fibers and emulsion. An emulsion-breaking agent is added and mixed therewith to precipitate the binder onto the fiber combination, where the precipitated binder is deposited onto the fibers within the mat. The powder is then added to that combination, with mixing, to dispose the powder on the binder and form a matting material. Thereafter, a mat is formed of that matting material, which constitutes the filter material of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a diagrammatic illustration of a layer of the filter material of the invention;

FIG. **2** is a highly idealized diagrammatic illustration of the binder on fibers of the filter material of FIG. **1** and adhering activated carbon powder thereto;

FIG. **3** is a diagrammatic illustration of a plurality of layers of FIG. **1** combined into a single filter media;

FIG. **4** also shows a plurality of layers of filter material forming a filter media, but with an enclosing top cover and bottom cover for cosmetic purposes;

FIG. **5** shows, in diagrammatic form, a closed end of a suitable filter media.

FIGS. **6**, **7** and **8** show embodiments of configurations of the filter material;

FIG. **9** shows the filter material in place on a pot for filtering tap water for producing a beverage;

FIG. **10** shows a conventional coffee making machine; and

FIGS. **11**, **12** and **13** show embodiments of disposition of the present filter material in a conventional coffee making machine.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

While, as noted above, the invention is adaptable to a variety of applications for gravity filtering of water for beverage use, and, as further noted above, the filter material of the invention will remove a number of contaminants from tap water, and the specification and claims should be so construed, for conciseness in this specification, the invention will be illustrated in terms of filters, primarily, useful in conventional coffee making machines and will reference, by example, chlorine removal from the filtered tap water.

As can be seen from FIG. **1**, the filter material comprises at least one layer of a mat, generally **1**, of laid fibers **2**. In this regard, the term "laid" is used in its common meaning, i.e. that the fibers have been laid (air laid or wet laid) onto a forming device, e.g. a screen, on which the fibers entangle into mat form. While in such conventional laying process, the fibers extend in all of the X, Y and Z directions of the mat, the fibers more generally are parallel to the forming surface, e.g. parallel to a screen on which the fibers are laid. Laid fibrous mats of this nature are conventionally made on conventional paper-making machines and are consolidated during the laying and forming steps, generally with further consolidation through pressure rolls, all of which is well known in the art and need not be recited herein in detail for purposes of conciseness. However, it is noted that within the meaning of the term "laid" is the condition that the mat is not a woven mat or a needled mat or a felted mat, but only a "laid" mat. It is important for purposes of the present invention that the mat be of laid fibers, since such laid fibers provide orientations of the fibers that are most useful in applying the binder, as described below, and in providing uniform filtration for removal of chlorine.

The fibers are selected from the group consisting of cellulosic fibers and synthetic textile fibers and mixtures thereof. Again, these terms are used in their ordinary sense, in that a textile fiber is, generally speaking, from about 1 to 20 deniers, capable of being formed into a textile, and may be of either continuous or staple form. Synthetic textile fibers are made from a variety of synthetic hydrophobic polymers. Thus, the textile fibers may be polyester fibers, nylon fibers, vinyl fibers, acrylic fibers, and the like, and the particular synthetic textile fiber is not critical to the invention. Inherent in this definition is that the fibers are non-porous and hydrophobic.

While cellulosic fibers may be in the form of textile fibers, that term also includes fibers which are not useful in forming textiles, but are more useful in forming paper and the like. Thus, the term "cellulosic fibers" includes not only fibers in a form suitable for textile formation, but suitable for paper making. The fibers may be cellulose fibers, modified cellulose fibers, and the like. The particular cellulosic fiber is not critical so long as the cellulose of the fibers has not been so modified that the fiber is no longer hydrophilic. Thus, within the definition of the term "cellulosic fibers" is included the requirement that the fibers are porous and hydrophilic.

As can be seen from FIG. **2**, deposited on the fibers **2** is a synthetic hydrophilic food-grade latex binder **3**. That binder, preferably, substantially covers the entire surface area of the fibers in layer **1**, as shown in FIG. **2**, and is in an amount sufficient to so bind the fibers together within the mat, e.g. at crossover points **4**, that during a filtration of cold water through the layer(s) **1** of the mat no substantial amount of fibers **2** are detached therefrom. In addition, the amount of binder must be insufficient to reduce a gravity flow rate of cold water through the mat to less than about 0.3 liters per minute per 100 square centimeters of the mat, since, otherwise, the gravity flow rate of cold water through the mat would not be sufficient to supply an ordinary and conventional coffee maker with sufficient water for making coffee at the usual rate of that coffee maker.

As also shown in FIG. **2**, a water insoluble chlorine adsorbent or absorbent solid powder **5** (in particle form) is disposed on the binder **3** such that no more than 65% of the total outside surface area of the powder is substantially contacted by the binder, as shown in FIG. **2**. Also as shown in FIG. **2**, portions of the particles do contact and are submerged or embedded into the sticky binder **3**, but portions of the particles **5** protrude out of the binder **3** and are free from and do not substantially contact the binder. Those protruding portions are, therefore, available for contacting water passing through the filter and adsorbing and/or absorb-

ing contaminants, especially chlorine, therefrom. In addition, since activated carbon has a multitude of inner-connected passageways inside the particles 5, by providing this unimpeded outer surface of the powder, sufficient total surface area (outside and inside surface area) is provided to remove contaminants from the water and to move those contaminants deep into the passageways of the particles of powder, even thought deeper passageways of the particles are submerged within the binder.

As shown in FIG. **3**, a plurality of layers **1** may make a filter media, generally **10**, and five such layers **1** are shown in FIG. 3. Generally speaking, however, if multiple layers are used, as opposed to only one layer, there will be at least 2 and up to 20 layers in a filter media **10**, but more preferably there are about 3 to 7 layers of the mat in a filter media.

FIG. **4** shows an optional embodiment where three layers **1** of the mat are contained within a top cover **11** and a bottom cover **12**. The coverings **11**, **12** are not required, but since, as explained below, the layers **1** will contain substantial amounts of activated carbon, which is black in color, and which color will show through the layers **1**, the covers **11** and **12** may be used simply for cosmetic or appearance purposes to hide the black color of the layers. This is because some users would object to a black filter for filtering water for beverage purposes.

The fibers of the mat of layers **1** may be all cellulosic fibers or all synthetic textile fibers or a mixture of cellulosic fibers and synthetic textile fibers. Alternately, one layer **1** of the mat may be all cellulosic fibers and another layer **1** of the mat be all synthetic textile fibers, with yet a further layer of the mat being a mixture of synthetic textile fibers and cellulosic fibers. In other words, alternating layers, as shown in FIG. **3**, may have various compositions of the synthetic textile fibers, the cellulosic fibers or mixtures thereof. When there is a mixture of the cellulosic fibers and the synthetic textile fibers, the ratio thereof can be as desired, but, generally speaking, it is preferable that the mixture have a preponderance of cellulosic fibers, e.g. where the weight percent of the synthetic fibers is from about 1 to 20%, especially about 5 to 15%, since these ranges give better results, especially where the synthetic fibers are the preferred fibers, i.e. an acrylic fiber or a polyester fiber.

While, as noted above, it is preferable that the binder substantially cover all of the surface area of the fibers, in certain applications it may be desirable to have less than such coverage, especially where the filter material is intended for complicated configurations and bendings. In such case, for example, only 60% or 70% or, perhaps, 80% of the surface area of the fibers is covered by a binder, and when a synthetic fiber is in the composition, that uncovered portion of the synthetic fiber will present a hydrophobic surface. This will decrease the flow rate, and, in that case, it is preferred that a solid food-grade surfactant is disposed within the mat, and more preferably disposed within the binder itself. This will provide less surface tension to the water being filtered and still maintain the appropriate flow rate. When such a solid food-grade surfactant is used, preferably, about 0.1 to 2% thereof is used, based on the weight of the mat. A suitable surfactant is Dow-Corning Q2-5247, which is a silicone food-grade surfactant.

A wide variety of synthetic fibers may be used, including acrylic fibers, polyester fibers, nylon fibers, olefin fibers, and vinyl fibers, and the particular synthetic fiber is not critical, especially when essentially covered with a binder or when a surfactant is used. However, as noted above, acrylic fibers and polyester fibers are preferred.

Likewise, the cellulosic fiber is not critical and may be cellulose fibers, methylcellulose fibers, rayon and cotton fibers, although cellulose fibers are preferred.

While the latex binder, again, can be chosen from a wide variety of binders, including an acrylic latex, a vinyl latex, an acrylonitrile latex, and an acrylate latex, the preferred latex is an acrylic latex, and especially a modified polyacrylic polymer latex. Such latex is commercially available under the trademark HYCAR sold by B. F. Goodrich. HYCAR 26083 is a particularly good latex in this regard and is a self-crosslinking carboxylated latex with excellent abrasion resistance. It forms a film with substantial clarity. However, other acceptable latexes are vinyl latexes, nitrile latexes, styrene-butylene latexes, also sold by B. F. Goodrich under the trademarks GEON, HYCAR and GOOD-RITE. Nevertheless, for the reasons noted above, the acrylic latex is preferred.

While the amount of binder should be as described above, for most of the latexes immediately described above, the amount of the binder in the mat is from about 5% to 40% based on the weight of the mat, and more preferably about 10% to 30%.

The water-insoluble chlorine adsorbent or absorbent solid powder, as noted above, also absorbs other contaminants, but for sake of conciseness in this specification, the contaminants are illustrated as chlorine. That powder, therefore, may be a variety of powders, such as diatomaceous earth, fuller's earth and the like, but for substantial and desired reductions in chlorine content of the filtered water, the powder is activated carbon. The activated carbon may be activated carbon per se, or impregnated with silver or nickel so as to increase the bacterial static property of the activated carbon. In this regard, since the binder is a food-grade binder, it is, by definition, a binder which will not support bacterial growth and is referred to as bacterially static, i.e. the amount of bacterial growth that will occur on the binder is not significant from a human health point of view. Thus, in order to complement the bacterial static property of the binder, the powder should also be bacterially static. While activated carbon is essentially bacterially static, at least for reasonable times of use, for certain waters, e.g. those high in bacterial nutrients or bacterial content, it may be advisable to use nickel- or silver-impregnated activated carbon, since these increase the bacterial resistance of the activated carbon and ensures that bacterial static property.

The amount of the powder contained in a mat will depend upon the amount of contaminants to be removed from the filtered water, the number of times a mat is envisioned for repeated and time spaced-apart use, and the ability of the binder to hold amounts of the powder firmly and substantially non-detachably thereto. In this latter regard, certain binders can so retain different amounts of the powder. Therefore, with some of the binders, the amount of the powder should not be more than about 20%, based on the weight of the mat, while with other of the binders, up to about 70% of the powder may be used in the mat, again based on the weight of the mat. With the preferred acrylic binder, as briefly noted above, that binder presents a very sticky surface and is capable of retaining large amounts of powder, e.g. activated charcoal, up to 70%, based on the weight of the mat. However, more usually, that percentage will be between about 40% and 60%, and more ideally about 50%. However, for high removal of chlorine, the amount of the powder should be more than 40%.

The amount of chlorine that can be removed from the powder, of course, will depend upon the average particle

size of the powder. For purposes of the present specification, a powder is defined as a solid adsorbent or absorbent having an average particle size of less than 2,000 microns, but more preferably the average particle size will be less than 1,000 microns, and more preferably less than 100 microns, so as to maximize chlorine removal, in view of the larger outer and internal surface areas provided per weight amount of the powder with decreasing particle size.

By use of such sticky binder to retain both the fibers and the powder so that they do not pass from the filter material, and by use of the present bacterially static components, a mat of filter material may be used for up to 50 time spaced-apart filtrations, i.e. time spaced apart sufficiently that substantial bacterial growth could take place between uses, as in daily use of a coffee maker. This must be, also, without significant displacement of either fibers or activated carbon from the filter and into the water for beverage purposes. That number of filtrations, of course, will depend upon the number of layers, the amount of activated carbon, and the particular binder, but even with a small number of layers and with other than the most preferred binder, i.e. the acrylic binder, at least up to 50 such filtrations may so take place. Even with only one layer, and especially with the preferred binder, the mat will remain substantially bacterially static for up to 10 time spaced-apart filtrations, and this is particularly true where the binder substantially covers the surfaces of the fibers in the mat, and more especially where the binder is substantially continuous over the fibers of mat.

Turning again to the drawings, FIG. **5** shows a single layer **1** with covers **11**, **12** and sealed edges **13**, e.g. by heat welding, gluing, etc. FIG. **6** shows the filter material in the form of a cone **60**, which could be used, for example, to filter water into a pitcher for removing chlorine in preparation of frozen orange juice, or that configuration could be used for preparing coffee in a coffee maker which consists essentially of a filter holder and a pot, where the coffee is placed in the filter holder and hot water is poured therethrough. Alternatively, a filter media may be made in the form of a disk **70**, as shown in FIG. **7**, with a number of layers **1** of filter material forming that disk **70**. In this case, the edges **71** of the disk **70** will normally be gathered together and sealed, as in FIG. **5**, so as to make the composite of the layers a somewhat unitary structure. This sealing, again, can be by gluing, heat sealing, ultrasonic welding, and the like, and the particular means of sealing is not critical to the invention.

As a further embodiment, the filter material may be a pleated filter **80**, as shown in FIG. **8**, having a plurality of pleats **81** held in a holder **82** to retain those pleats.

As yet a further alternative, as shown in FIG. **9**, the filter material **90** may be in something of a conical disk shape **91** for fitting over the top of the conventional pot **92** for filtering water therethrough.

FIG. **10** shows a conventional coffee making machine with a housing **100** having a cold water reservoir **101**, a coffee-containing basket compartment **102**, a coffee pot **103** and a heated hot plate **104**.

FIG. **11** shows that same coffee making machine **100** having the pleated filter **80** of FIG. **8** disposed in the bottom of the cold water reservoir **101**. That pleated configuration can be so disposed by way of a water-tight drawer (not shown) removable from the reservoir or can be simply placed at the bottom of the reservoir by manual insertion.

FIG. **12** shows the same coffee making machine **100** with the cone filter **60** of FIG. **6** fitted into the upper portion of the cold water reservoir **101**. Preferably, in this case, the cone will have a peripheral bead (not shown) of an elastomer, such as rubber, to make the filter material **60** more secure therein.

FIG. **13** shows that same coffee machine **100** having a disk **70**, as shown in FIG. **7**, placed at the bottom of the cold water reservoir, and again, either by a water-tight drawer (not shown) or by manual insertion.

The filter material is made by the following method. The fibers, as described above, are mixed with water to form a dispersion of the fibers in the water. The latex binder, in the form of an emulsion (5% to 70% solids), is then added with mixing to the dispersion to form a dispersed mixture of fibers and emulsion. After sufficient mixing, an emulsion-breaking agent is added, with mixing, to the mixture to form a precipitated binder on the fiber combination, where the precipitated binder is deposited onto the fiber within the mat, as shown in FIG. **2**. Thereafter, to that combination is added the powder, with mixing, to dispose the powder onto the binder, again as shown in FIG. **2**, and form a matting material. That matting material is then formed into a mat by conventional paper-making processes, as briefly described above.

By first depositing the binder on the fibers, by such precipitation, and only thereafter depositing the powder on the binder, the powder is stuck to the binder, during mixing, as briefly described above, in such a manner that it is firmly attached to the binder within the mat, but, at the same time, a substantial amount of the outer surface area of a particle of the binder upstands from and is not contacted with the binder, again as shown in FIG. **2**. When the binder is a very sticky material, such as the preferred acrylic binder, substantial amounts of the powder can be disposed on the fibers (on the binder) to maximize chlorine removal from the water being filtered.

The emulsion-breaking agent is not critical and will depend, in part, on the particular emulsion in which the binder is dispersed. The combination of the latex and fibers, naturally, exhibit overall negative charges. Therefore, unless this natural condition is altered, the latex particles of the emulsion will not precipitate. This natural charge, and hence stability of the latex emulsion, can be broken by adjusting the pH of the latex emulsion and/or neutralizing the natural negative charge. Alum, for example, can both lower the pH and neutralize the natural negative charge and, hence, is a preferred emulsion-breaking agent. Alum, as well as other compounds, provides accessible positive charges for breaking the latex emulsion. Alternatively, modified starches are cationic and, thus, will provide positive charges for emulsion breaking. Starches will also enhance the dry strength of the formed mat and, thus, are a preferred agent.

It is also useful to provide a viscosity control agent in the mix the enhance the mat forming process. Gums, such as Karaya gum, are useful in this regard.

Conventional retention aids, such as Cartaretin AEM (an acrylamide), can be used to assure that all of the fibers and powder remain in the mat during the forming step.

Since emulsions are normally pH sensitive, as noted above, the binder emulsion can be broken by the adding thereto of a base to lower the pH. Any of the usual bases are useful, and the particular base is not critical.

The amount of the emulsion-breaking agent will, of course, depend upon the particular emulsion and the particular binder therein, but, generally speaking, the amount need be only that amount which will lower the pH or neutralize the negative charge to that emulsion-breaking point. For most emulsions, however, a pH of below about 4 will be sufficient for breaking that emulsion.

As noted above, the viscosity control agents are useful in the mixing processes and in depositing the mixture onto a formacious surface, such as a screen, for producing the laid mat. The viscosity control agent may be added in amounts up to about 2% or 3% and any of the conventional viscosity control agents may be used, e.g. gums, and the preferred gum is Karaya gum.

With the preferred embodiments, i.e. the acrylic binder, activated carbon, and the mode of placing that activated carbon on the binder, as explained above, gravity flow rates of at least 0.5 liter per minute per 100 square centimeters of the mat can easily be obtained, and flow rates even up to 5 liters per minute per 100 square centimeters of mat are obtainable. This is a very significant and high gravity flow rate, which makes the present filter material an ideal material for producing filter media for coffee pots and the like, as described above. Gravity flow is defined as the flow rate of water through the filter with no more than one foot of static head pressure on the water.

The invention will now be illustrated by the following examples, but it is to be understood that the examples are not limiting thereof but merely illustrate the same. In the examples, as in the specification and claims, all percentages and parts are by weight, unless otherwise specified.

EXAMPLE 1

This example illustrates a method of producing the filter material. The apparatus used in this example is a conventional paper-making machine, the details of which need not be described herein, for sake of conciseness, since those details are well known to those skilled in the art.

Preparation of Starch and Alum

Using a 1000 ml beaker on top of a Corning hot plate and a G. K. Heller heavy duty laboratory stirrer with a series "H" motor controller @ a speed of 500 rpm, add 32 g Cato 2A starch to 500 mls of cold water, heat to 200° F. for 30 min., turn heat off, add 32 g alum and 300 mls of cold water. Total amount of solution 800 mls.

Preparation of Gum

Using a 1000 ml beaker on top of a Corning hot plate and a G. K. Heller heavy duty laboratory stirrer with a series "H" motor controller @ a speed of 500 rpm, heat water (615 mls) to 180° F., then add 3.67 g triethanolamine and 1.76 g ammonia (gum dispersing agents), then slowly add 8 g Karaya gum; add 185 g cold water, agitate for 5 min. @ a speed of 250 rpm. Total amount of solution 800 mls.

Preparation of Flocculant

Using a 500 ml beaker and a G. K. Heller heavy duty laboratory stirrer with a series "H" motor controller @ a speed of 250 rpm, add 6.3 g Cartaretin AEM liquid to 393.7 ml of water. Total amount of solution 400 mls.

Preparation of the Matting Material

Using a small Osterizer 12-speed blender with 700 mls of water, pulp 9 g (dried) bleached Kraft softwood pulp (cellulose fibers—"HP11"—Trademark of Buckeye Cellulose) on "high" (liquify selection button) for 30 seconds, stop blender; add 2.8 g acrylic fiber and pulp an additional 30 seconds. Transfer slurry to 1800 ml beaker. Using a G. K. Heller heavy duty laboratory stirrer with a series "H" motor controller @ a speed of 200 rpm, add 5.7 g of B. F. Goodrich 26083 latex with 5.7 g water; add 15 g of Starch and Alum solution, wait 2 min., add 27.4 g gum solution; in the above blender using 400 ml of water, add 11.8 g activated carbon; run on low speed for 5 seconds and transfer to slurry rinse with 50 ml of water, agitate for 2 min., then add 4.2 g. of Flocculant solution and transfer to handsheet mold which has a water level of 12.5 liters; while stirring slurry pull vacuum switch to form sheet, with 24 inch vacuum. Open cover of handsheet mold, take out formed sheet and use a vacuum machine (Dayton wet & dry) for additional removal of moisture; transfer sheet to an Emerson speed dryer—temp setting 270° F.—wait until dry (10 min.).

EXAMPLE 2

Using a small Osterizer 12 speed blender with 700 mls of water, pulp 11.8 g staple polyester fiber on "high" (liquify selection button) for 60 seconds. Transfer slurry to 1800 ml beaker. Using a G. K. Heller heavy duty laboratory stirrer with a series "H" motor controller @ a speed of 200 rpm, add 5.7 g of B. F. Goodrich 26083 latex with 5.7 g water; add 15 g of Starch and Alum solution, wait 2 min., add 27.4 g gum solution; in the above blender using 400 ml of water, add 11.8 g activated carbon run on low speed for 5 seconds and transfer to slurry rinse with 50 ml of water, agitate for 2 min., then add 4.2 g of Flocculant solution and transfer to handsheet mold which has a water level of 12.5 liters; while stirring slurry pull vacuum switch to form sheet, with 24 inch vacuum. Open cover of handsheet mold and take out formed sheet and use a vacuum machine (Dayton) for additional removal of moisture; transfer sheet to an Emerson speed dryer—temp. setting 270° F.—wait until dry (10 min.).

EXAMPLE 3

This example demonstrates the dechlorination abilities of the filter material produced by Example 1. In this test 20 cc. per minute of distilled water containing 10 to 11 ppm chlorine were continuously injected through a sample holder containing 10 layers of 1 inch diameter filter material produced according to Example 1. The 10 layers of mat were placed in a sample cell and the cell closed and tightened. At a flow rate of 20 cc. per minute, the residual chlorine was tested at 10 minute intervals using a HACH testing method DR2000 Program #80 for a period of 1 hour. The residual chlorine in parts per million was as follows:

Time-Minutes	Chlorine Residual
10	.01
20	.01
30	.01
40	.01
50	.03
60	.04

As can be seen from the above results, the present filter material has considerable capabilities for removing chlorine and reduces the chlorine content from 10 to 11 ppm to 0.01 ppm for up to 40 minutes and with no more than 0.04 ppm for up to 60 minutes, which would translate into the equivalent of about 80 pots of brewed coffee with more than 80% chlorine removal efficiency.

EXAMPLE 4

This example shows the flow rate produced by the filter media of Example 1. One layer of the filter media was placed in a 4⅜ inch diameter by 2½ inch high disk sample holder.

500 ml of distilled water was passed through the above sample holder by pouring to measure the flow rate. The flow rate obtained was 500 ml in 65 seconds.

As a comparison a filter material identical to that of Example 1, with the exception that the filter material had a conventional non-hydrophilic acrylate binder and not the present hydrophilic binder, was likewise tested. Without the present hydrophilic binder, the fibers remained hydrophobic. The flow rate in that sample was 3 ml in 150 minutes.

As can be seen, this second flow rate test shows that conventional fibers or filter materials with conventional hydrophobic properties have a very low flow rate and are not acceptable for uses such as in coffee making machines, but with the present invention, flow rates quite acceptable for such conventional coffee making machines are obtainable.

What is claimed is:

1. A filter material for removing chlorine from cold water used in preparing a human-consumable beverage, comprising:

(a) at least one layer of a mat of laid fibers selected from the group consisting of cellulosic fibers and synthetic textile fibers and mixtures thereof;

(b) a synthetic hydrophilic, food-grade latex binder deposited onto the fibers within the mat in an amount sufficient to so bind the fibers together within the mat that during a filtration of cold water through the mat no substantial amount of fibers are displaced therefrom and in an amount insufficient to substantially reduce a gravity flow rate of cold water through the mat to less than about 0.3 liter per minute per 100 square centimeters of said mat; and

(c) a water-insoluble chlorine adsorbent or absorbent solid powder disposed on said binder such that no more than 65% of the total surface area of the powder is substantially contacted by said binder.

2. The filter material of claim 1 wherein there are from 2 to 20 layers of said mat.

3. The filter material of claim 2 wherein there are from 3 to 7 layers of said mat.

4. The filter material of claim 1 wherein the fibers are all cellulosic fibers.

5. The filter material of claim 1 wherein the fibers are all synthetic textile fibers.

6. The filter material of claim 1 wherein the fibers are a mixture of cellulosic fibers and synthetic textile fibers.

7. The filter material of claim 6 wherein the weight percent of synthetic fibers is from about 1% to 20%.

8. The filter material of claim 7 wherein the weight percent of synthetic fibers is from about 5% to 15%.

9. The filter material of claim 8 wherein the synthetic fiber is an acrylic fiber.

10. The filter material of claim 9 wherein a solid food-grade surfactant is disposed within the mat.

11. The filter material of claim 10 wherein the amount of the solid food-grade surfactant is from 0.1% to 2% based on the weight of the mat.

12. The filter material of claim 1 wherein the synthetic fibers are selected from the group consisting of acrylic fibers, polyester fibers, nylon, olefin fibers and vinyl fibers.

13. The filter material of claim 1 wherein the cellulosic fibers are selected from the group consisting of cellulose fibers, methylcellulose fibers, rayon and cotton fibers.

14. The filter material of claim 1 wherein the latex binder is selected from the group consisting of an acrylic latex, a vinyl latex, a nitrile latex and an acrylate latex.

15. The filter material of claim 1 wherein the binder is an acrylic latex.

16. The filter material of claim 1 wherein the amount of binder in the mat is from about 5% to 40%, based on the weight of the mat.

17. The filter material of claim 16 wherein the amount of binder in the mat is from about 10% to 30%, based on the weight of the mat.

18. The filter material of claim 1 wherein said gravity flow rate is at least 0.5 liter per minute per 100 square centimeters of said mat and up to 5 liters per minute per 100 square centimeters of mat.

19. The filter material of claim 1 wherein the powder is activated carbon.

20. The filter material of claim 19 wherein the powder is silver- or nickel-impregnated activated carbon.

21. The filter material of claim 1 wherein the amount of powder in the mat is from 20% to 70%, based on the weight of the mat.

22. The filter material of claim 21 wherein said percentage is between about 40% and 60%.

23. The filter material of claim 1 wherein no more than about 50% of the total surface area of the powder is substantially contacted by said binder.

24. The filter material of claim 23 wherein said percentage is no more than 40%.

25. The filter material of claim 1 wherein the average particle size of the powder is less than 1,000 microns.

26. The filter material of claim 25 wherein the average particle size is less than 100 microns.

27. The filter material of claim 1 wherein the mat is substantially bacterially static for up to 50 filtrations.

28. The filter material of claim 1 wherein the mat is substantially bacterially static for up to 20 filtrations.

29. The filter material of claim 1 wherein the mat is substantially bacterially static for up to 10 filtrations.

30. The filter material of claim 1 wherein the binder substantially covers the surfaces of the fibers in the mat.

31. The filter material of claim 30 wherein the binder is substantially continuous over the fibers of the mat.

32. A method for making the filter material of claim 1, comprising:

(a) mixing the fibers in water to form a dispersion of the fibers in the water;

(b) adding and mixing the latex binder in the form of an emulsion to the dispersion to form a dispersed mixture of the fibers and emulsion;

(c) adding and mixing an emulsion-breaking agent to the mixture to form a precipitated binder on the fibers combination where the precipitated binder is deposited onto the fibers within the mat;

(d) adding to the combination and mixing the powder with the combination to dispose the powder onto the binder and form a matting material; and

(e) forming a mat of the matting material.

33. The method of claim 32 wherein the agent is alum.

34. The method of claim 33 wherein the alum is added with a starch.

35. The method of claim 32 wherein a viscosity control agent is added to the combination before the powder is added thereto.

36. The method of claim 35 wherein the viscosity control agent is a gum.

37. The method of claim 36 wherein the gum is Karaya gum.

* * * * *

United States Patent [19]

Sugino et al.

[11] Patent Number: 5,071,700

[45] Date of Patent: Dec. 10, 1991

[54] CARBON FIBER-REINFORCED CARBON COMPOSITE MATERIAL

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[73] Assignee: Kabushiki Kaisha Kobe Seiko Sho, Kobe, Japan

[21] Appl. No.: 594,057

[22] Filed: Oct. 9, 1990

Related U.S. Application Data

[62] Division of Ser. No. 177,082, Apr. 4, 1988, Pat. No. 4,983,451.

[30] **Foreign Application Priority Data**

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[52] U.S. Cl. 428/283; 423/447.1; 423/447.2; 428/244; 428/284; 428/300; 428/298; 428/367; 428/368; 428/402; 428/408

[58] Field of Search 428/283, 244, 406, 408, 428/402, 408, 902, 367, 368, 300, 284, 298; 423/447.1, 447.2

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Primary Examiner—James J. Bell

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[57] **ABSTRACT**

Disclosed herein are a carbon fiber-reinforced carbon composite material composed of carbon as a matrix and carbon fiber as a reinforcement, and also a process for producing the same. The composite material is produced by coating nonwoven fabrics of carbon fiber or a blend of carbon fiber and organic fiber with a filler-containing liquid, laminating the nonwoven fabrics one over another, and subjecting the laminated nonwoven fabrics to needle punching repeatedly with a plurality of needles, thereby yielding a prepreg of three-dimensional structure, and carbonizing and calcining the thus obtained prepreg.

4 Claims, 1 Drawing Sheet

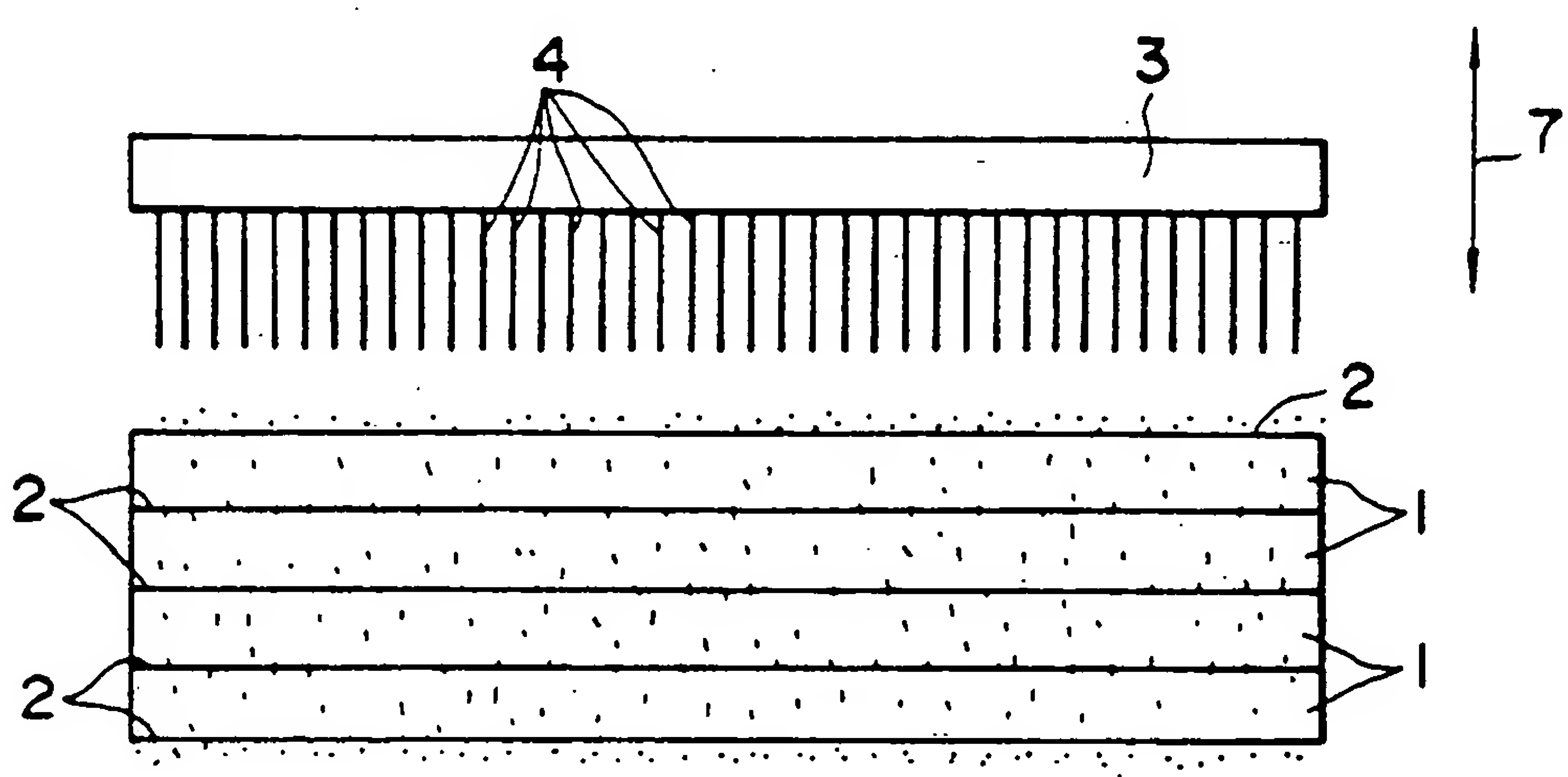


FIGURE 1

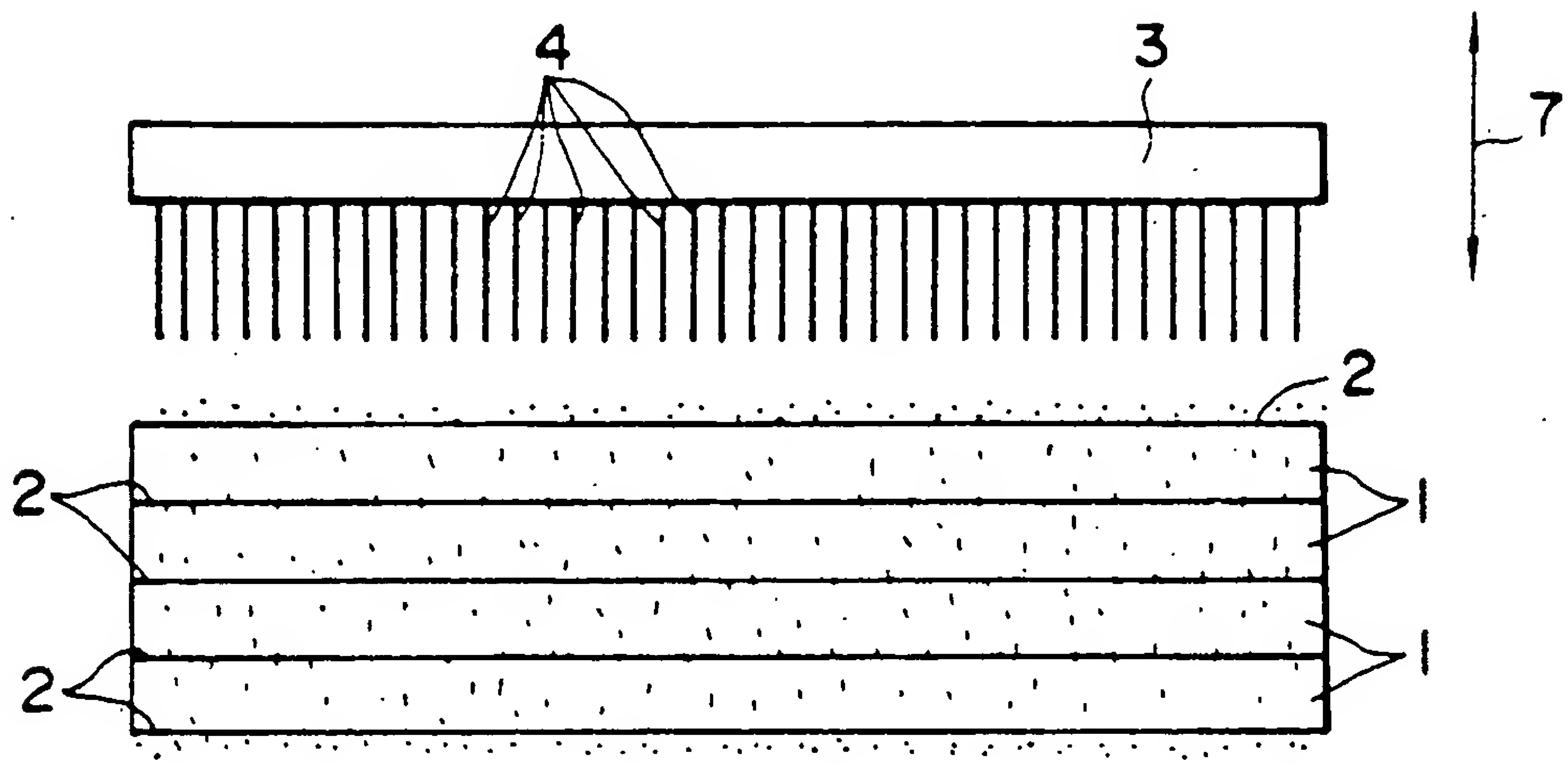
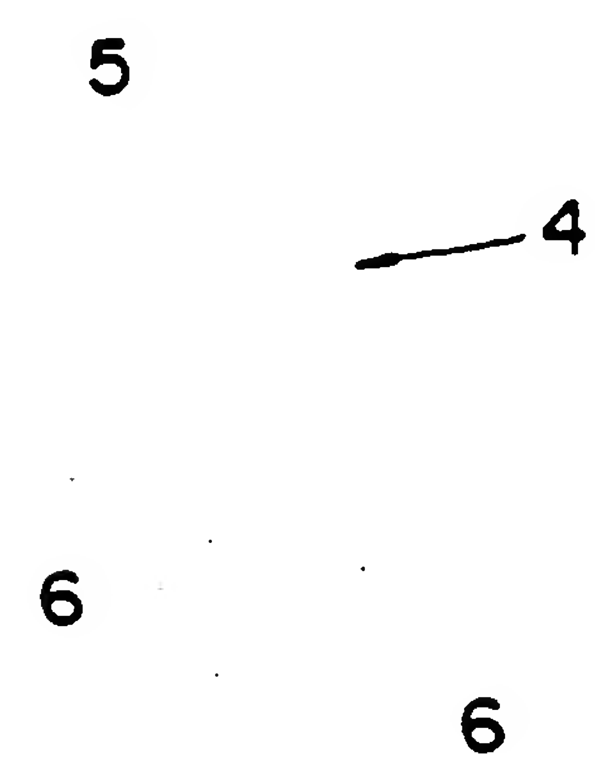


FIGURE 2



CARBON FIBER-REINFORCED CARBON COMPOSITE MATERIAL

This is a division, of application Ser. No. 07/177,082, filed on Apr. 4, 1988 now U.S. Pat. No. 4,983,451.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a carbon fiber-reinforced carbon composite material composed of carbon as a matrix and carbon fiber as a reinforcement, and also to a process for producing the same.

2. Description of the Prior Art

Carbon fiber-reinforced carbon composite material is referred to as C/C material. It is used as a heat-resistant material in the fields of spacecraft and aircraft. The process for producing the C/C composite material is disclosed in U.S. Pat. Nos. 3,734,797 and 4,201,611; British Patent No. 1,360,887; Japanese Patent Laid-open Nos. 62768/1974 and 101985/1979; and Japanese Patent Publication No. 25094/1987. According to one of the disclosed processes, the C/C composite material is produced in the following manner. At first, a perform of nonwoven fabric or woven fabric is impregnated or coated with pitch or a thermosetting resin such as phenolic resin, furan resin, and epoxy resin, thereby to form a prepreg. A plurality of the prepregs are laminated on top of the other to form a multi-layer product. The layers are made into a unified body by press molding or the like. The unified body is calcined so that the matrix resin is carbonized and graphitized. If necessary, the impregnation and calcination are repeated to increase the density of the composite material. According to the other disclosed process, the C/C composite material is produced by the steps of laminating nonwoven fabrics by needle punching, thereby forming a preform, impregnating the preform with a resin, and calcining and carbonizing the impregnated preform.

The above-mentioned process has a disadvantage that the pitch or thermosetting resin does not permeate into the filament yarns (composed of 1000 to 4000 filaments) which constitute the nonwoven fabric or woven fabric. Thus the resulting C/C composite material is liable to cracking at the fiber-matrix interface and also to delamination. Moreover, the C/C composite material produced by the above-mentioned process has locally unbalanced strength which leads to delamination and deformation during use.

In order to overcome these disadvantages, a new C/C composite material has been developed. It is produced by mixing a matrix raw material (such as thermosetting resin) with short fiber to give a prepreg, and molding and calcining the prepreg. The thus produced short fiber-reinforced carbon composite material is poor in strength and impact resistance because the fiber region is small and the fiber-to-fiber distance is large. An additional disadvantage of this composite material is that the strength in the direction parallel to the surface is smaller than that in the direction perpendicular to the surface.

SUMMARY OF THE INVENTION

The present invention was completed to overcome the above-mentioned disadvantages. Accordingly, it is an object of the present invention to provide a carbon fiber-reinforced carbon composite material which has an increased strength in the direction parallel to the surface of the laminated nonwoven fabric and also meets the requirements for large-sized complex-shaped products. It is another object of the present invention to provide a process for producing the carbon fiber-reinforced carbon composite material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating the process used in an example of the invention.

FIG. 2 is a schematic diagram illustrating the structure of the needle.

DETAILED DESCRIPTION OF THE INVENTION

The carbon fiber-reinforced carbon composite material pertaining to the present invention is produced by coating nonwoven fabrics of carbon fiber or a blend of carbon fiber and organic fiber with a filler-containing liquid, laminating the nonwoven fabrics one over another, and subjecting the laminated nonwoven fabrics to needle punching repeatedly with a plurality of needles, thereby yielding a prepreg of three-dimensional structure, said filler-containing liquid being composed of a base liquid of synthetic resin liquid and one or more than one kind of filler selected from graphite powder, carbon black powder, carbon short fiber, graphite short fiber, synthetic resin powder, pitch powder, mesophase pitch powder, coke powder, ceramics powder, metal powder, metal short fiber, Si_3N_4 whisker, SiC whisker, and ceramics short fibers.

According to the process of the invention, nonwoven fabrics containing carbon fiber which are placed one over the other undergo needle punching, with the filler-containing liquid interposed between them. The needle punching forces the liquid into the nonwoven fabric in the thickness direction, with the result that the filler applied to and supported on fibers is sufficiently distributed in the thickness direction. Moreover, the needle punching causes carbon fibers and filler to orient in the thickness direction at the interface between the nonwoven fabrics placed one over the other. The oriented carbon fibers and filler greatly increase the resistance to delamination. Incidentally, needle punching can be applied to any large-sized or complex-shaped carbon fiber-reinforced composite material to impart uniform strength and performance by properly arranging the number and distribution of needles.

The present invention was completed on the basis of findings obtained in the present inventors' experiments carried out to achieve the object of the present invention. In the first experiment, nonwoven fabrics placed on top of the other was subjected to needle punching to prepare a nonwoven fabric of such structure that fibers run in the thickness direction and holes are made in the direction perpendicular to the interlayer. The needle-punched nonwoven fabric was then impregnated with a liquid containing a filler such as carbon powder, $Si3N_4$, and SiC whisker, followed by calcination. The steps of impregnation and calcination were repeated. It was found that the powdery filler suspended in the liquid does not permeate the nonwoven fabric but stays on the surface of the nonwoven fabric. It was also found that it is difficult to obtain a high-density product because the nonwoven fabric containing a large amount of carbon fibers is limited in basis weight on account of resistance to needle punching. Nonwoven fabrics of low basis weight easily deform during impregnation and calcination, giving no products of desired dimensions. In the

second experiment conducted to overcome these disadvantages, nonwoven fabrics were subjected to needle punching after they were coated with a filler-containing liquid. It was found that the needle punching forces the filler into the nonwoven fabric and distributes it at a sufficiently high density in the thickness direction.

An embodiment of the present invention will be explained with reference to the accompanying drawing. FIG. 1 is a schematic representation illustrating the method pertaining to the present invention. In FIG. 1, there is shown a nonwoven fabric 1 which is composed of carbon fibers or a blend of carbon fibers and organic fibers. According to the process of the present invention, the surface of the nonwoven fabric 1 is coated with a filler-containing liquid 2, and the coated nonwoven fabrics (four sheets in the illustrated embodiment) are laminated one over another. The filler-containing liquid is composed of a base liquid of synthetic resin and a filler dispersed therein. The filler is carbon, metal, ceramics, synthetic resin, or a blend thereof in the form of powder, whisker, or short fiber which serves as a reinforcement for the carbonaceous matrix. Examples of the filler include graphite powder, carbon black powder, carbon short fiber, phenolic resin powder, epoxy resin powder, pitch powder, mesophase pitch powder, coke powder, metal powder and short fiber (e.g., stainless steel, nickel, steel, aluminum, brass, and cast iron), Si_3N_4 whisker, SiC whisker, and ceramics short fibers. They are used alone or in combination with one another. The nonwoven fabric 1 should preferably have a basis weight of 5 g/m^2 or above. With a basis weight lower than 5 g/m^2, the nonwoven fabric is too loose to be coated satisfactorily.

The filler-containing liquid 2 may be in the form of paste as well as liquid. Its coating weight is 0.5 to 300 times the weight of the nonwoven fabric. With a coating weight less than 0.5 times, the effect of the filler is not satisfactory. With a coating weight in excess of 300 times, the filler spoils the performance of the nonwoven fabric.

Needles 4 are set in a flat support 3. As shown in FIG. 2, each needle 4 has a shank 5 and barbs 6 projecting outward from the shank 5. The needles 4 should preferably be set at a density of 5 needles/cm^2 or above. Otherwise, the needles do not catch as many carbon fibers as necessary for the sufficient distribution of the filler in the thickness direction.

Needle punching is accomplished by reciprocatively moving the needles 4 vertically with respect to the surface of the nonwoven fabric 1 (in the direction shown by the arrow 7) so that the needles 4 are forced into the laminated nonwoven fabrics 1 repeatedly. Needle punching causes carbon fibers to be arranged vertically with respect to the surface of the nonwoven fabric. Needle punching also forces the filler into the nonwoven fabric 1 because each layer of the nonwoven fabrics 1 is coated with the filler-containing liquid 2. After needle punching, the filler is oriented in the thickness direction of the nonwoven fabrics 1 and a portion of the filler is present across the interface of the nonwoven fabrics as schematically shown in FIG. 1.

The needles should preferably be pushed in the direction perpendicular to the surface of the nonwoven fabric; however, the pushing direction may be inclined within 45 degrees without any adverse effect on the object of the present invention. If the needles are inclined more than 45 degrees, the desired effect of needle punching is not produced because the pushed needles tend to slip along the surface of the nonwoven fabric.

After a series of needle punching, a plurality (say, 4 sheets) of additional nonwoven fabrics 1 which have been coated with the filler-containing liquid are placed on the punched nonwoven fabrics 1, and needle punching is repeated so that carbon fibers and filler are distributed in the thickness direction of the nonwoven fabrics 1. In this way there is obtained a prepreg of three dimensional structure in which a prescribed number of nonwoven fabrics 1 are integrally laminated.

Subsequently, this prepreg is densified by the application of isostatic pressure of 500 kgf/cm^2 or above. With a pressure lower than 500 kgf/cm^2, the resulting product will not have satisfactory performance because the filler is not uniformly distributed.

Finally, the prepreg is dried and then cured at a proper temperature (say, 150° C.). After curing, the prepreg is carbonized and calcined in a furnace at a proper temperature (say, 1000° C.).

The thus obtained C/C composite material has the matrix of carbonaceous material formed by the carbonization and calcination of the synthetic resin constituting the base of the filler-containing liquid. If the synthetic resin is a thermosetting resin such as phenolic resin and epoxy resin, it forms vitreous carbon after carbonization and calcination. If the base contains graphite (soft carbon) or pitch and/or coke which becomes soft carbon upon calcination, there is obtained a matrix composed of vitreous carbon and soft carbon.

EXAMPLE 1

A nonwoven fabric having a basis weight of 200 g/m^2 was prepared from carbon fiber tow (having a tensile strength of 300 kg/mm^2) and polyester fiber by carding in a ratio of 80:20 by weight. The nonwoven fabric was cut to a size of 100 mm wide by 200 mm long. As many nonwoven fabrics as necessary were coated with a filler-containing liquid (in a paste form) of the formulation shown in Table 1.

TABLE 1

Filler-containing liquid	Filler: Graphite powder (wt %)	Filler: Phenolic resin powder (wt %)	Base liquid: Phenolic resin (wt %)
No. 1	—	50	50
No. 2	30	20	50
No. 3	50	—	50
No. 4	—	—	100

The paste-coated nonwoven fabrics were laminated on top of the other. Each time of lamination, the nonwoven fabrics underwent needle punching at a density of 10 needles/cm^2. Twenty layers of nonwoven fabrics were laminated. The thus obtained prepreg was heated for curing at 150° C. for 40 minutes, followed by calcination in a furnace at 1000° C. for 5 hours. Thus there was obtained a C/C composite material having a specific gravity of 1.5 g/cm^3 and a porosity of 10%. The physical properties of the thus obtained C/C composite materials are shown in Table 2.

TABLE 2

Filler-containing liquid	Density (g/cm^3)	Flexural strength (kgf/cm^2)	Compressive strength (kgf/cm^2): Thickness direction	Compressive strength (kgf/cm^2): Parallel to the surface
No. 1	1.40	1000	1530	1200
No. 2	1.48	1000	1400	1000

TABLE 2-continued

Filler-containing liquid	Density (g/cm^3)	Flexural strength (kgf/cm^2)	Compressive strength (kgf/cm^2) Thickness direction	Compressive strength (kgf/cm^2) Parallel to the surface
No. 3	1.50	900	1200	800
No. 4	1.35	600	700	400

It is noted from Table 2 that the C/C composite materials obtained from nonwoven fabrics coated with the filler-containing liquid Nos. 1, 2, and 3 pertaining to the present invention have a high density, a high flexural strength, and a high compressive strength (specially in the direction along the interface of the laminated layers). When it comes to sliding performance, the filler-containing liquid No. 3 is the best and No. 2 comes next, according to the braking test conforming to SAE J661. The thus obtained C/C composite material was not subject to delamination, swelling, and cracking.

EXAMPLE 2

A nonwoven fabric was prepared from carbon fiber and polyvinyl chloride fiber at a blending ratio of 90:10 by weight. The nonwoven fabric was cut to size as in Example 1. Twenty layers of nonwoven fabrics were laminated by repeating the application of the filler-containing liquid (Nos. 1 to 3 shown in Example 1) and the needle punching at a density of 10 needles/cm^2. As many nonwoven fabrics as necessary were coated with a filler-containing liquid (in a paste form) of the formulation shown in Table 1. Curing and calcination were carried out under the same conditions as in Example 1. The physical properties of the thus obtained C/C composite materials are shown in Table 3.

TABLE 3

Filler-containing liquid	Density (g/cm^3)	Flexural strength (kgf/cm^2)	Compressive strength (kgf/cm^2) Thickness direction	Compressive strength (kgf/cm^2) Parallel to the surface
No. 1	1.42	1200	1550	1250
No. 2	1.49	1000	1450	1100
No. 3	1.51	950	1300	900

In this example, there were obtained high-density, high-strength C/C composite materials which are not subject to delamination, swelling, and cracking.

EXAMPLE 3

A nonwoven fabric having a basis weight of 100 g/m^2 was prepared from carbon fiber and polyvinyl chloride fiber at a blending ratio of 90:10 by weight. The nonwoven fabric was cut to a size of 100 mm by 100 mm. Twenty layers of the nonwoven fabrics were laminated by repeating needle punching at a density of 5 needles/cm^2 or above, with each layer coated with a filler-containing liquid in the form of paste prepared by dissolving 100 g of phenolic resin powder in 100 g of furfuryl alcohol and incorporating the resulting solution with 50 g of graphite powder and 10 g of CF milled. Needle punching was repeated for several layers at one time. After the completion of needle punching, the upper and lower surfaces of the laminate were coated with the paste. The needle-punched laminate underwent cold isotactic pressing at 2000 kgf/cm^2, followed by drying at 100° C. or below for 3 days. The dried laminate underwent press molding at 180° C. and 50 kgf/cm^2. The resulting molded product was calcined in a nonoxidative atmosphere by raising the temperature at a rate of 10° C./hour or below until 500° C. and at a rate of 30° C./hour or below until 1000° C. Thus there was obtained a C/C composite material. The same experiment as above was repeated except that the formulation of the paste was changed as shown in Table 4. The characteristic properties of the thus obtained C/C composite materials are shown in Table 5.

TABLE 4

No.	Phenolic resin powder	Graphite powder	Third components: CF milled	SiC whisker	Wollastonite powder	Kaolin	Stainless steel fiber
1	100	50	10	—	—	—	—
2	100	50	—	10	—	—	—
3	100	50	—	—	10	—	—
4	100	50	—	—	—	10	—
5	100	50	—	—	—	—	10
6	100	50	—	—	—	—	20
7	100	50	—	—	—	—	30

Unit: parts by weight

TABLE 5

Paste No.	Density (g/cm^3)	Flexural strength (kgf/cm^2)	Compressive strength (kgf/cm^2) Thickness direction	Compressive strength (kgf/cm^2) Parallel to the surface
1	1.58	1050	1600	1100
2	1.55	950	1680	1050
3	1.63	750	1500	800
4	1.65	700	1450	800
5	1.70	1150	1650	1050
6	1.72	1100	1600	950
7	1.75	1000	1500	900

COMPARATIVE EXAMPLE

The same procedure as in Example 2 was repeated except that needle punching was not performed. The characteristic properties of the resulting C/C composite materials are shown in Table 6. It is noted that all the products are inferior to those in Examples 1 and 2. The product formed by applying the filler-containing liquid No. 1 delaminated and cracked during use, and the products formed by applying the filler-containing liquid Nos. 2 and 3 delaminated and cracked during the production process.

TABLE 6

Paste No.	Density (g/cm^3)	Flexural strength (kgf/cm^2)	Compressive strength (kgf/cm^2) Thickness direction	Compressive strength (kgf/cm^2) Parallel to the surface
1	1.30	650	950	400
2	1.38	550	900	400

TABLE 6-continued

Paste No.	Density (g/cm³)	Flexural strength (kgf/cm²)	Compressive strength (kgf/cm²) Thickness direction	Parallel to the surface
3	1.41	500	700	350

As mentioned above, the carbon fiber-reinforced composite material of the present invention has an extremely high strength in the direction along the surface because the filler in the form of powder, fiber, or whisker is added in the thickness direction in the layers and interfaces of nonwoven fabrics. The filler also contributes to the improvement of sliding performance of the composite material. Owing to the needle punching which unifies the laminated nonwoven fabrics, the composite material contains uniformly distributed reinforcement in the matrix. Thus, according to the method of the present invention, it is possible to produce easily a large-sized complex-shaped composite material.

What is claimed is:

1. A carbon fiber-reinforced composite material comprising:

a plurality of layers of non-woven fabric reinforcing material containing carbon fibers;

a carbonaceous matrix surrounding said reinforcing material; and

a carbon, metal, or ceramics filler in the form of powder, whiskers or short fibers which is dispersed in the carbonaceous material;

wherein the carbon fibers of said reinforcing material and said filler are oriented in the thickness direction at the interface between the non-woven fabrics.

2. A carbon fiber-reinforced carbon composite material as claimed in claim 1 wherein the carbonaceous matrix material is composed of vetreous carbon and soft carbon.

3. A carbon fiber-reinforced carbon composite material as claimed in claim 1, wherein the filler is one or more than one kind selected from graphite powder, carbon black powder, carbon short fiber, graphite short fiber, coke powder, metal powder, metal short fiber, ceramics powder, ceramics whisker, and ceramics short fiber.

4. A carbon fiber-reinforced carbon composite material as claimed in claim 1, wherein the amount of filler is 0.5 to 300 times that of the reinforcing material.

* * * * *

US005134030A

United States Patent [19]

Ueda et al.

[11] **Patent Number: 5,134,030**

[45] **Date of Patent: Jul. 28, 1992**

[54] **PACKING MATERIAL AND PACKING MADE OF THE SAME**

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[73] Assignee: **Nippon Pillar Packing Co., Ltd.**, Osaka, Japan

[21] Appl. No.: **216,908**

[22] PCT Filed: **Nov. 25, 1987**

[86] PCT No.: **PCT/JP87/00909**

§ 371 Date: **Jun. 15, 1988**

§ 102(e) Date: **Jun. 15, 1988**

[87] PCT Pub. No.: **WO88/04004**

PCT Pub. Date: **Jun. 2, 1988**

[30] **Foreign Application Priority Data**

Nov. 25, 1986 [JP] Japan 61-280968

[51] **Int. Cl.**^{5} **D04C 1/00**; D06P 7/00

[52] **U.S. Cl.** **428/365**; 428/224; 428/289; 428/367; 428/377; 428/408; 57/230; 57/231; 57/232; 277/230; 277/DIG. 6; 87/1; 87/6; 87/9

[58] **Field of Search** .... 428/224, 367, 365, 377, 428/397, 408; 57/230, 231, 232; 277/230, DIG. 6; 87/1, 6, 9

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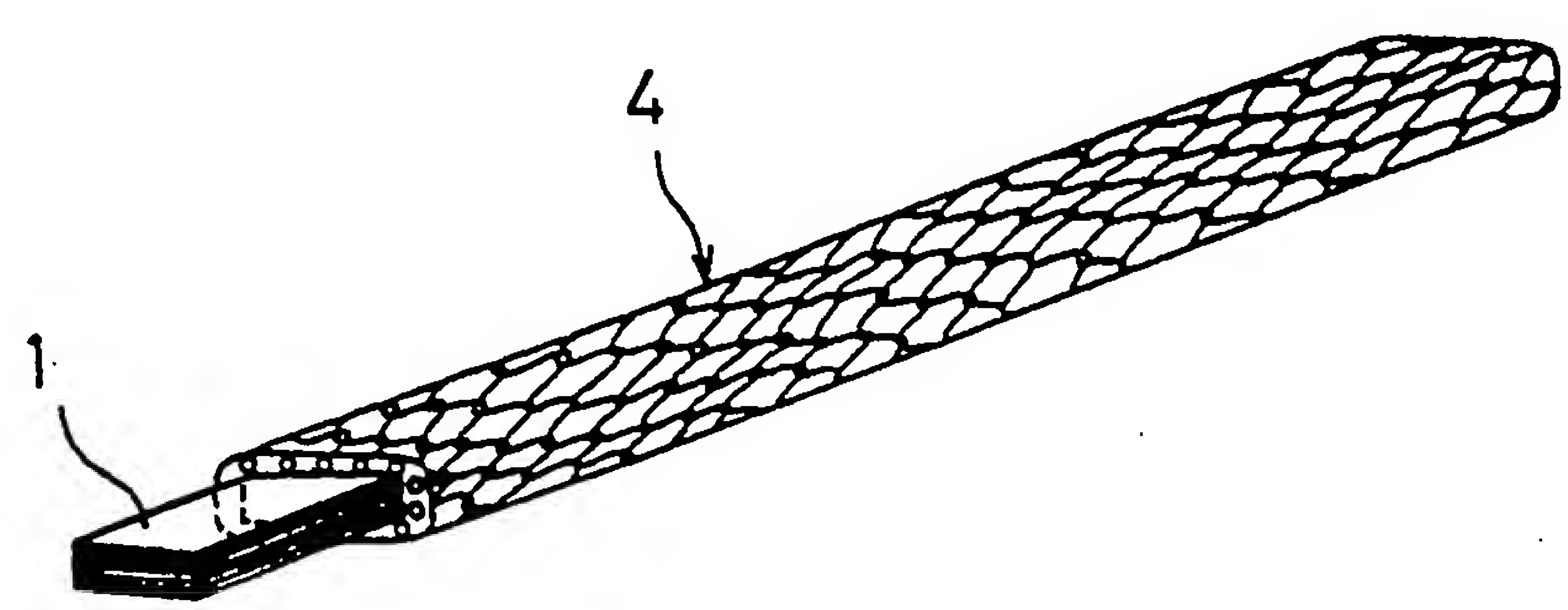
Primary Examiner—George F. Lesmes
Assistant Examiner—Christopher Brown
Attorney, Agent, or Firm—Jones, Tullar & Cooper

[57] **ABSTRACT**

This invention relates to a packing used in sealing two members. As the packing material, by using a material having the surface of a flexible graphite sheet cut to a width of less than 5 mm with fibers, or a material prepared by laminating a flexible graphite sheet cut to a width of less than 5 mm with at least one of reinforcing fiber of foil material, and covering its surface with fibers, or a material prepared by impregnating a principal component composed of flexible graphite particles with at least one of short fiber, rubber, resin or lubricant to form a bar-like structure and covering its surface with fibers, a packing material which can be either twisted or braided is obtained. By fabricating a packing by using any one of such packing materials, a cord-like packing is obtained without having to produce many packings matched to the dimensions of the members.

51 Claims, 6 Drawing Sheets



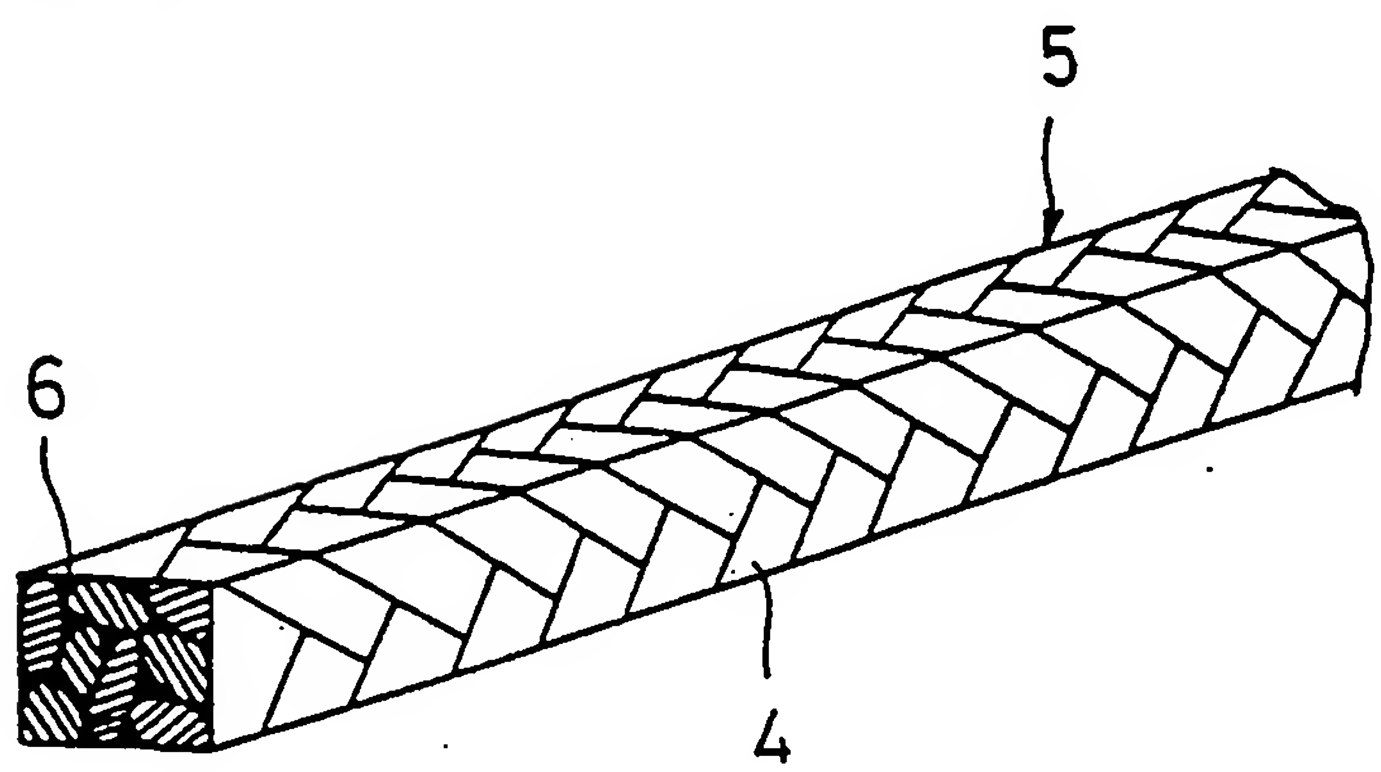


Fig. 1

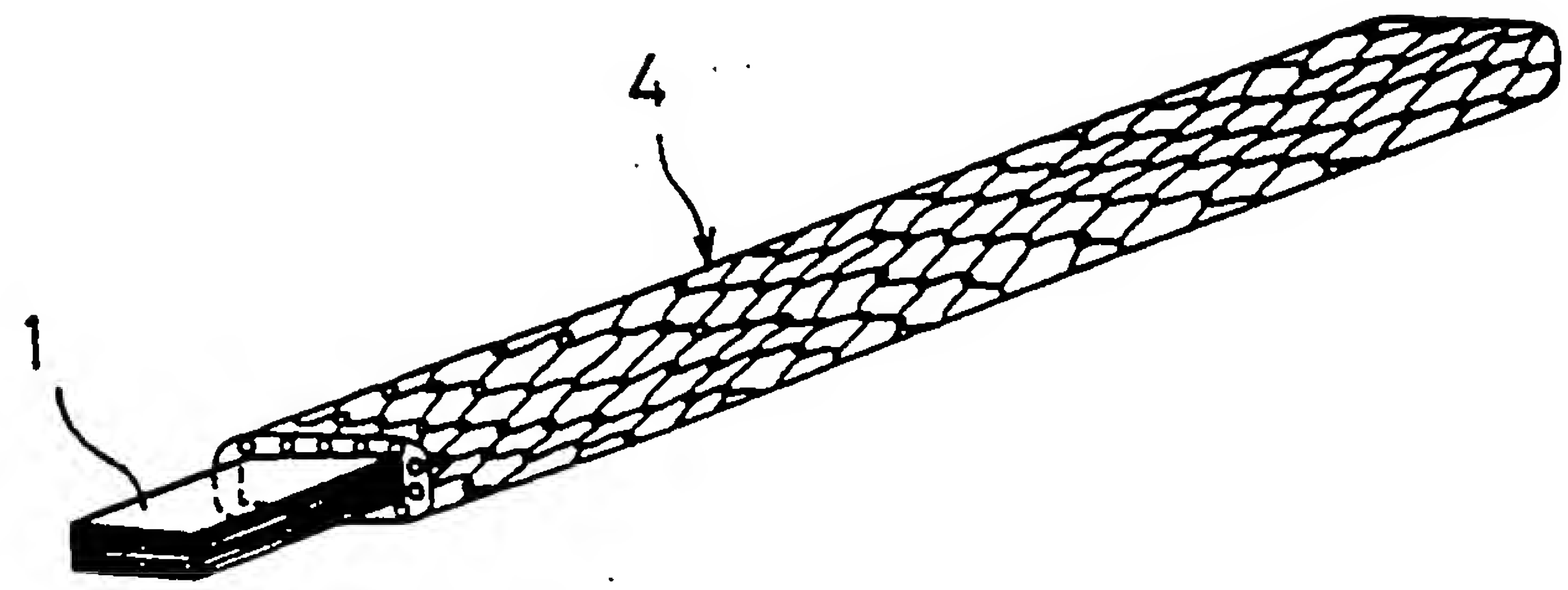


Fig. 2

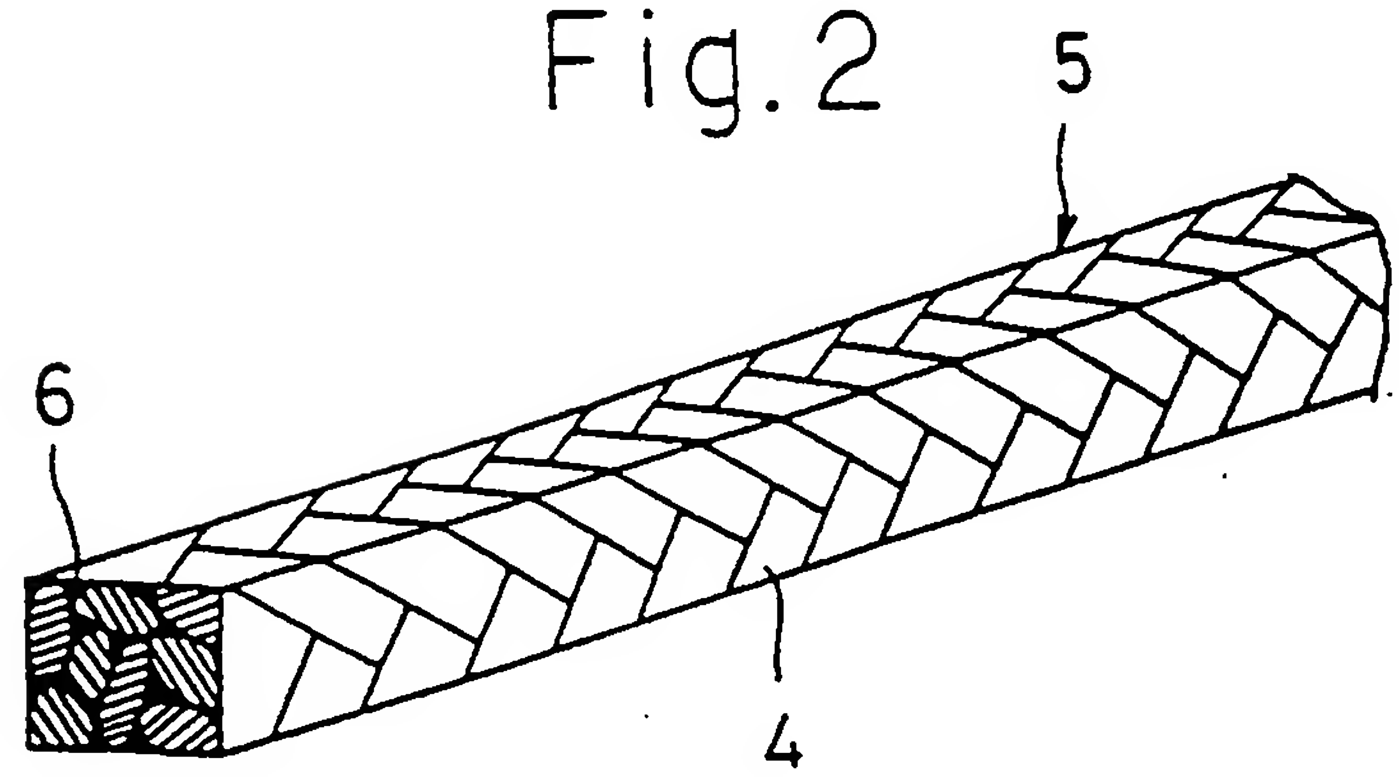


Fig. 3

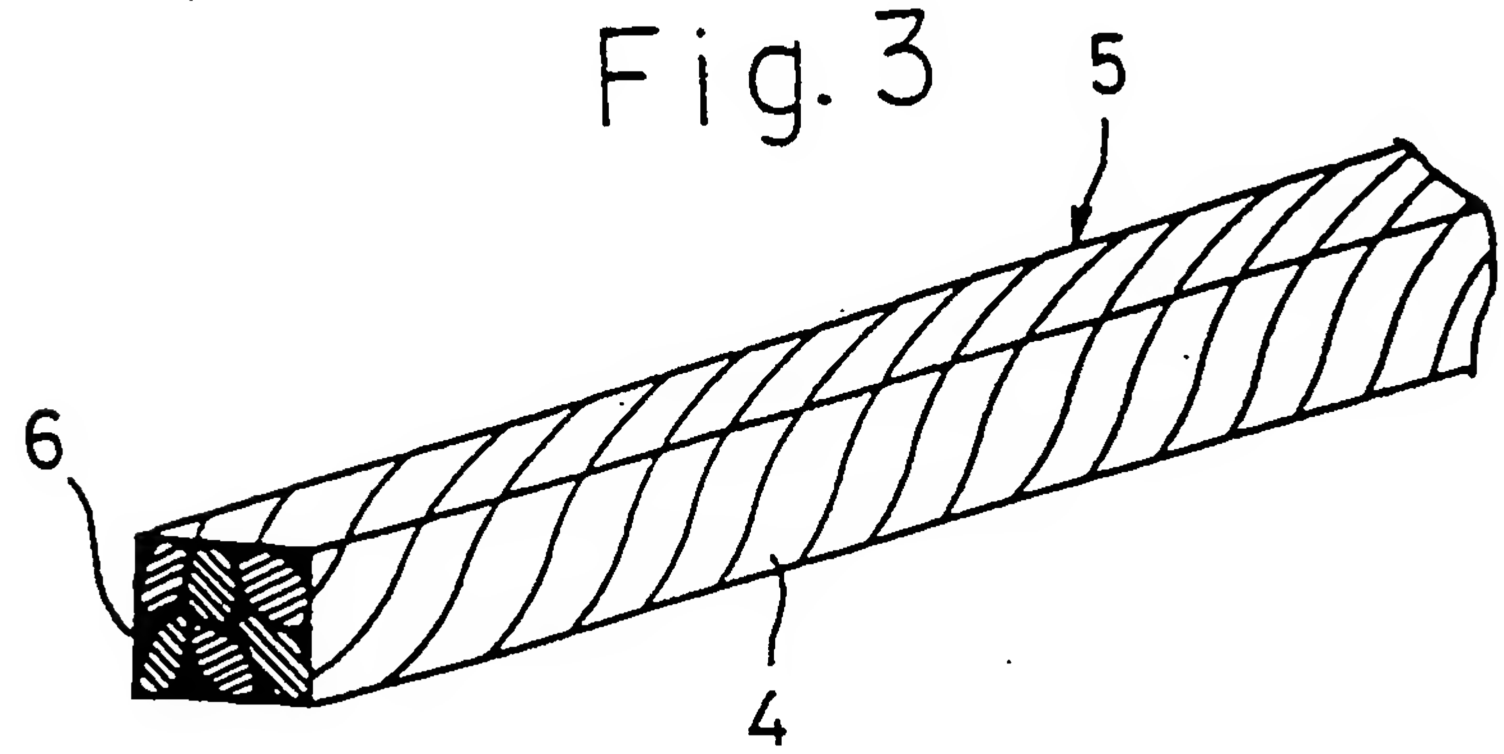


Fig. 4

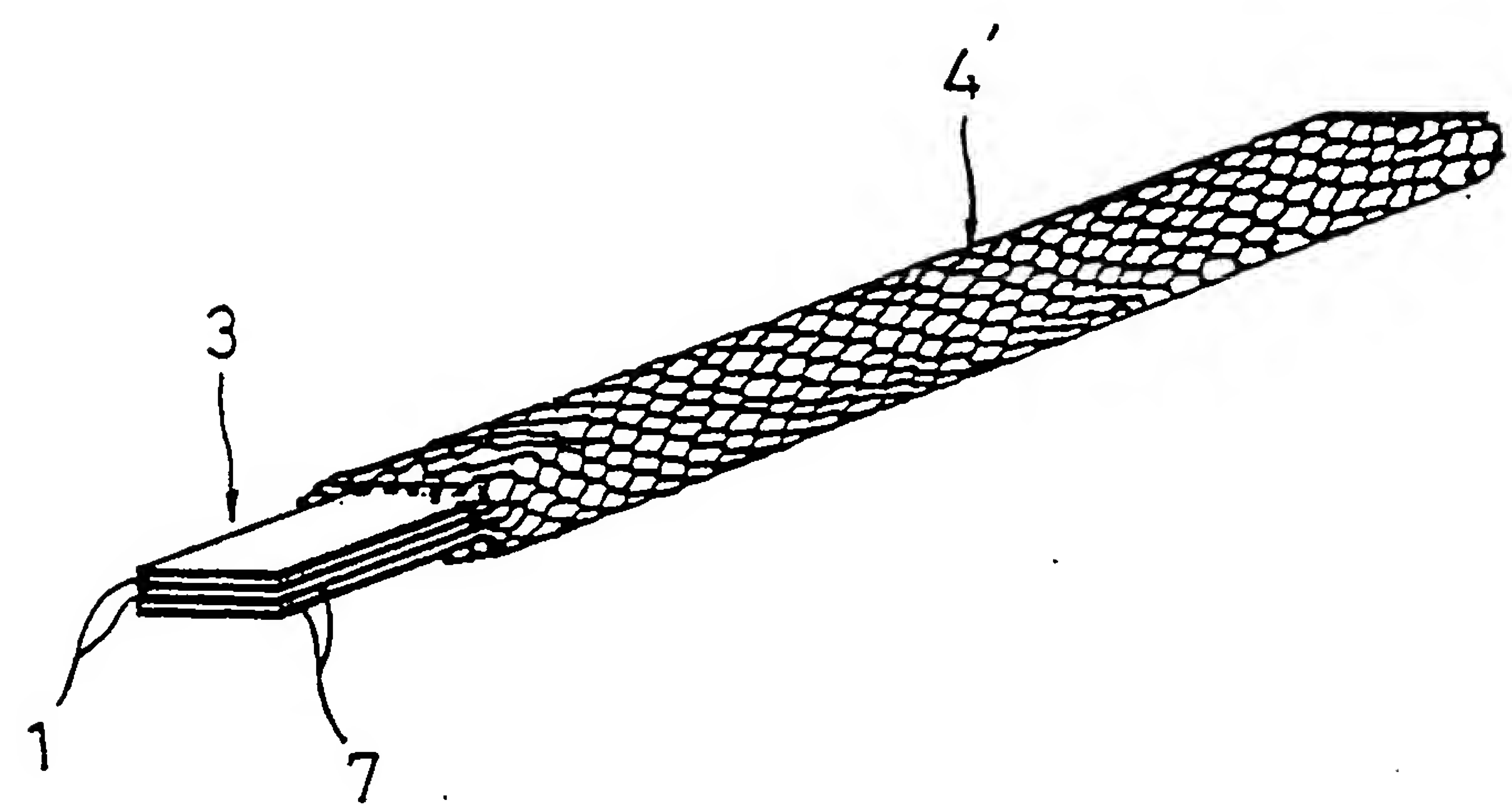


Fig. 5

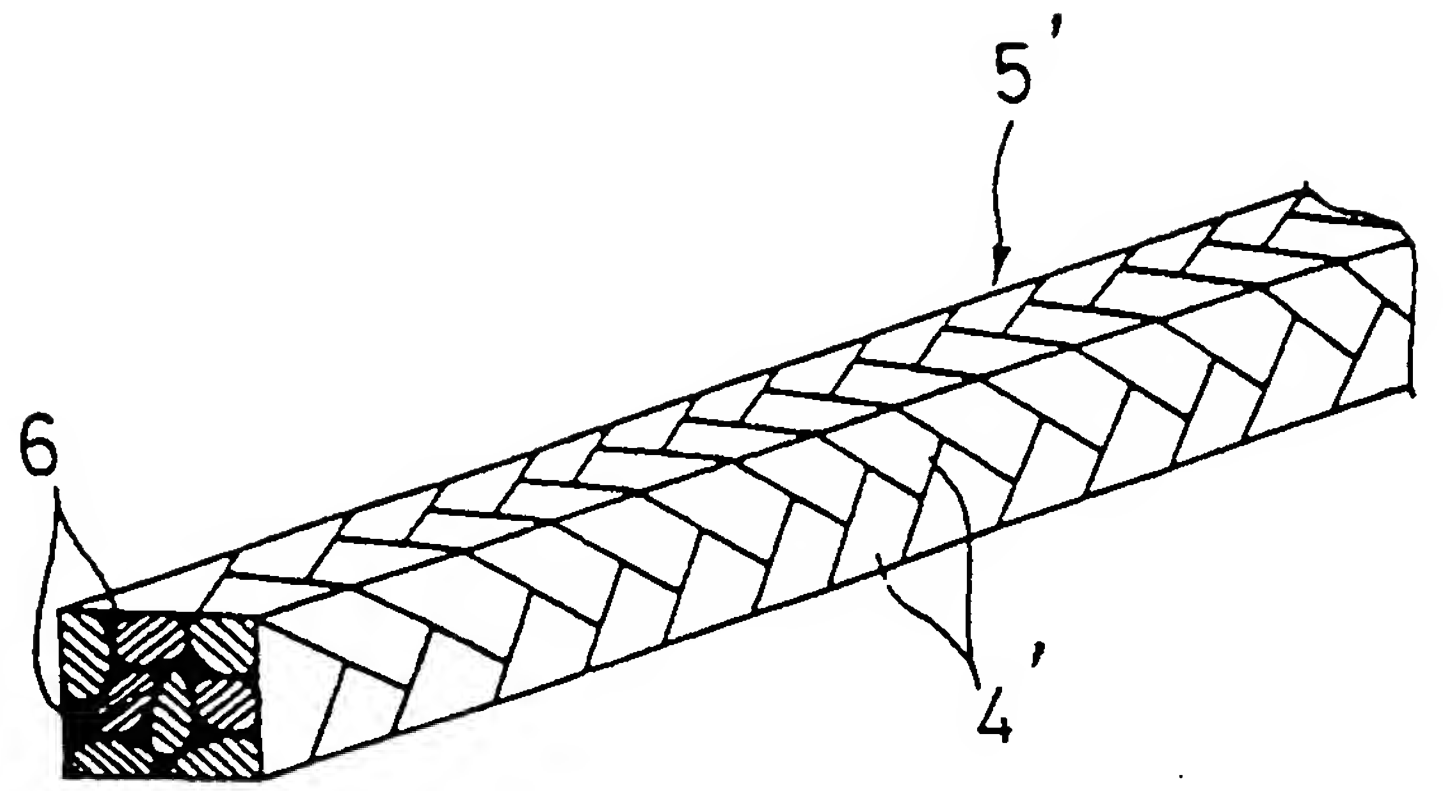


Fig. 6

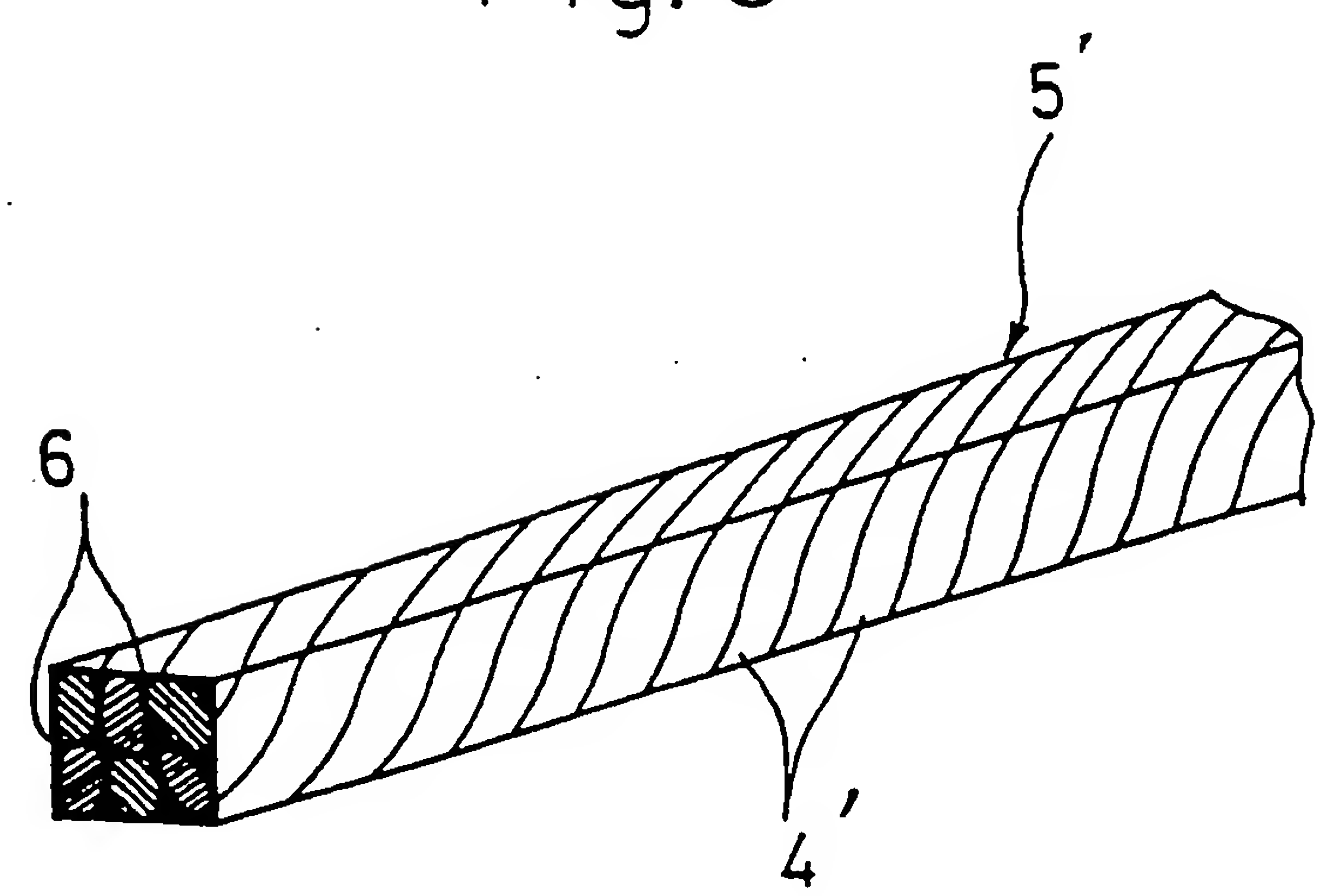


Fig. 7

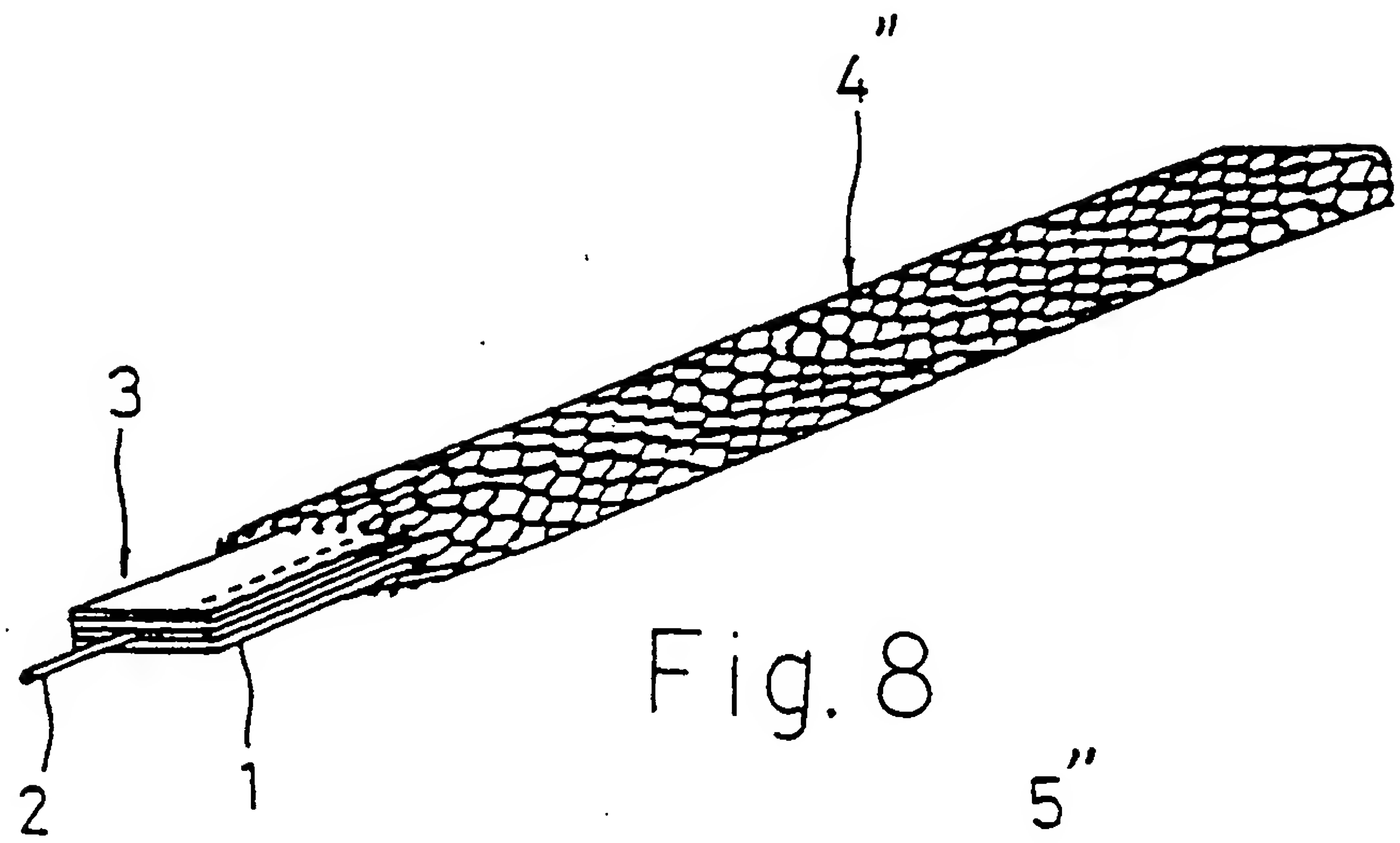


Fig. 8

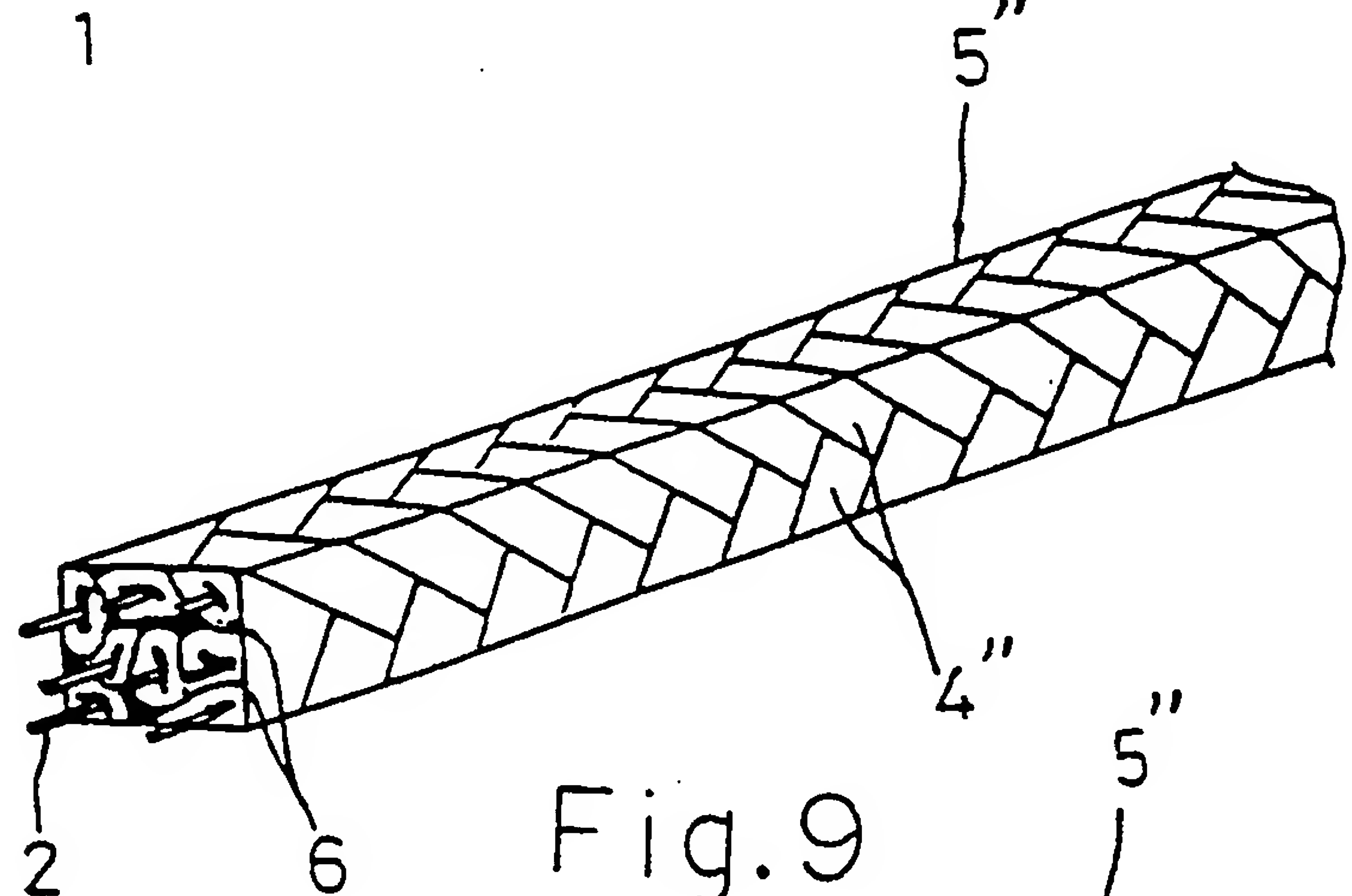


Fig. 9

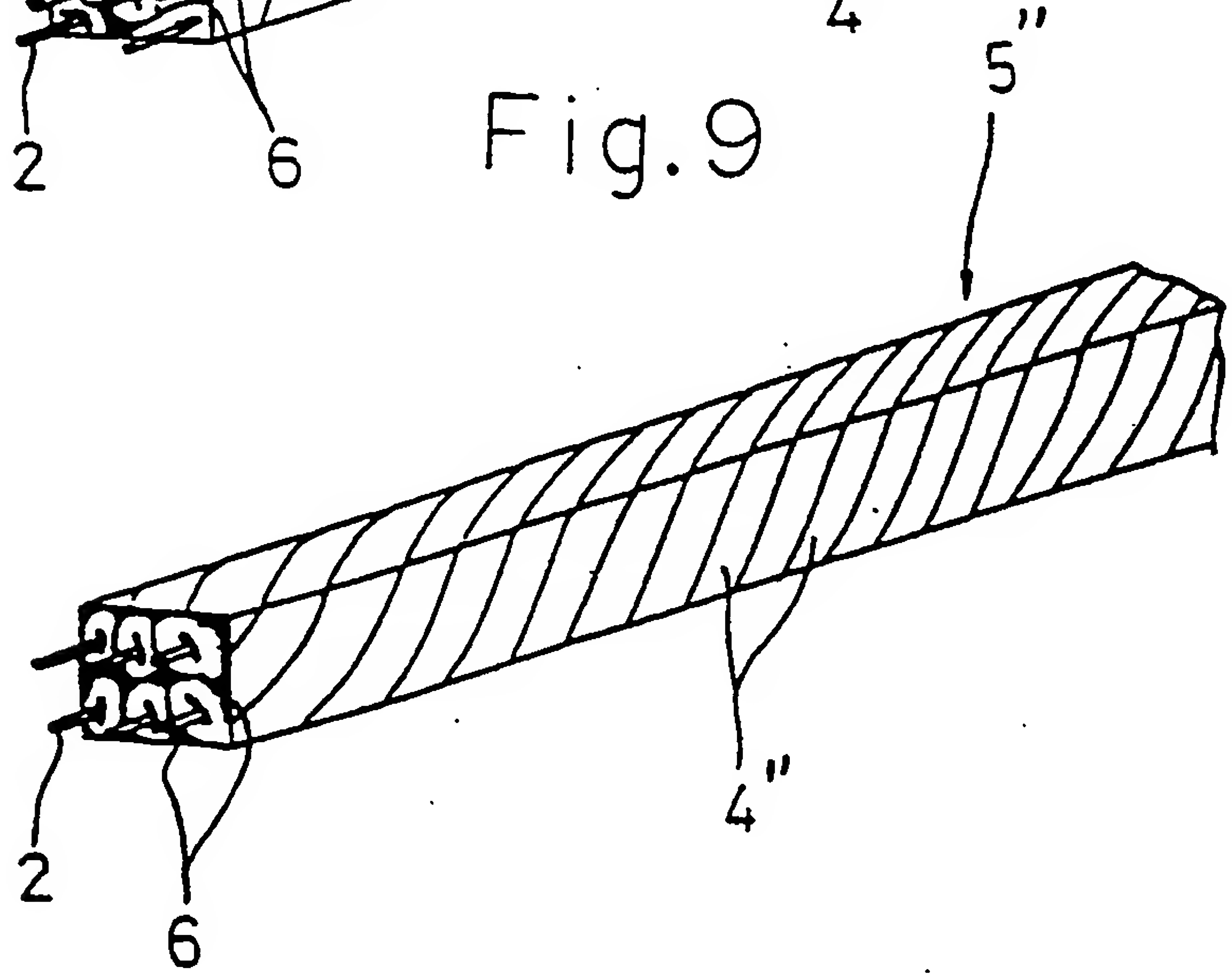


Fig.10

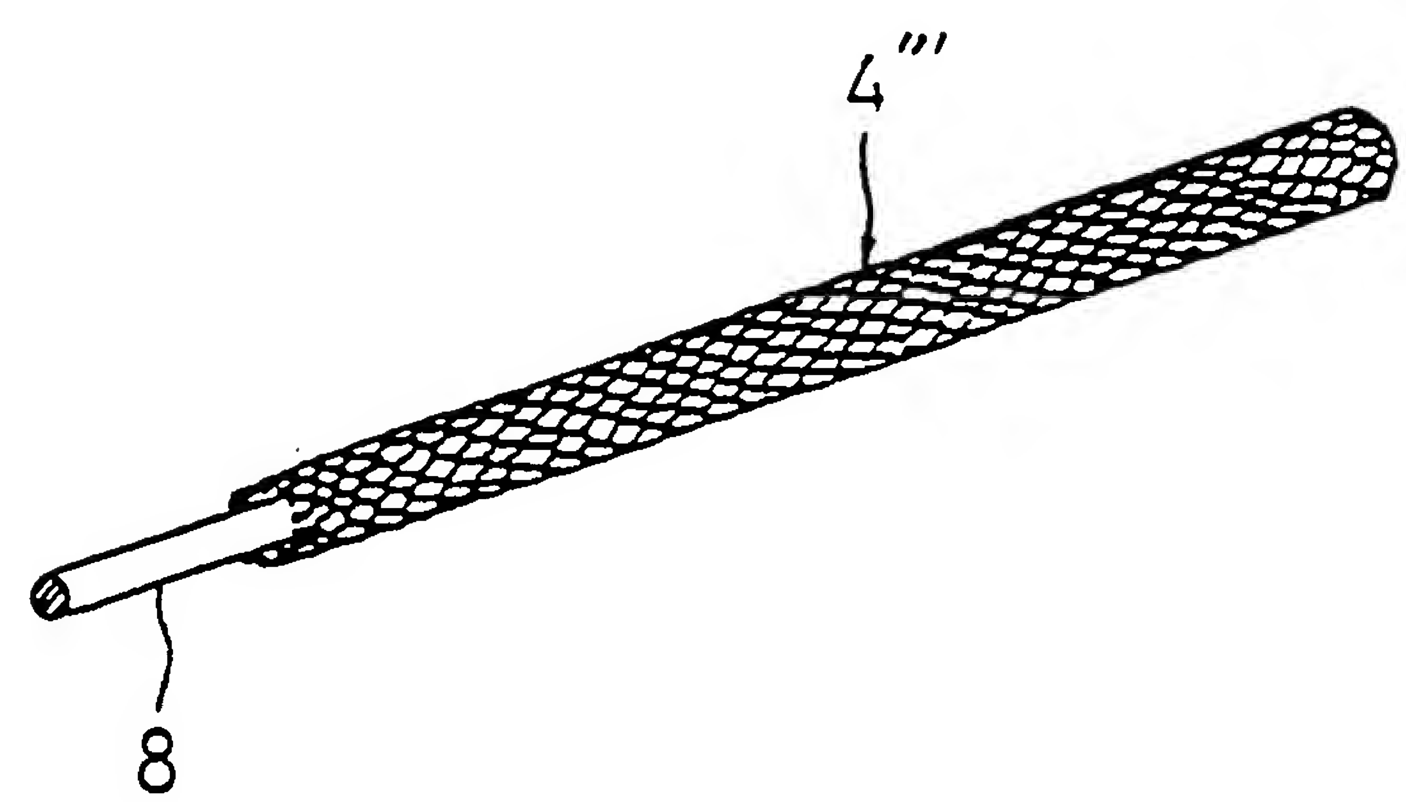


Fig. 11

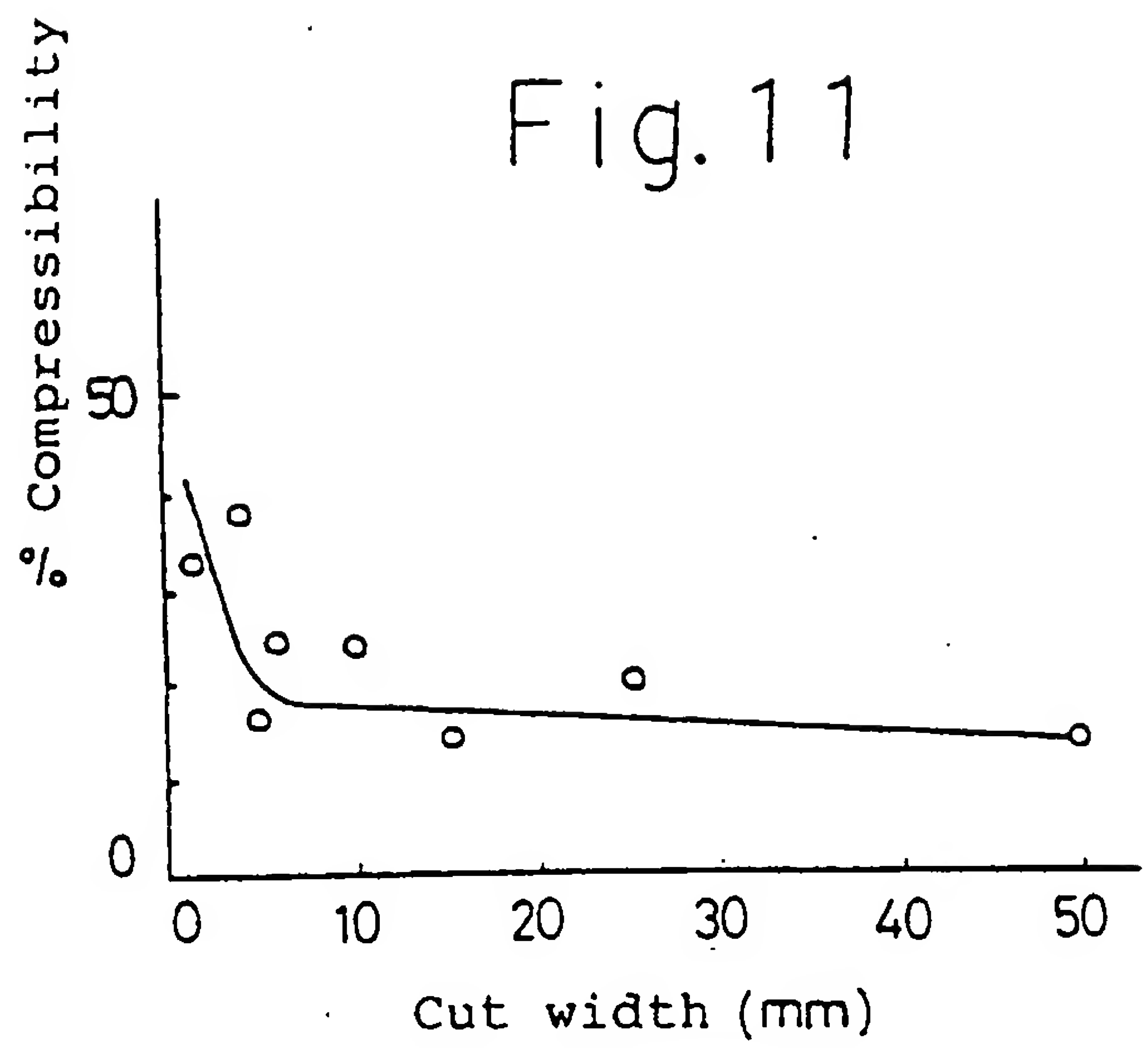
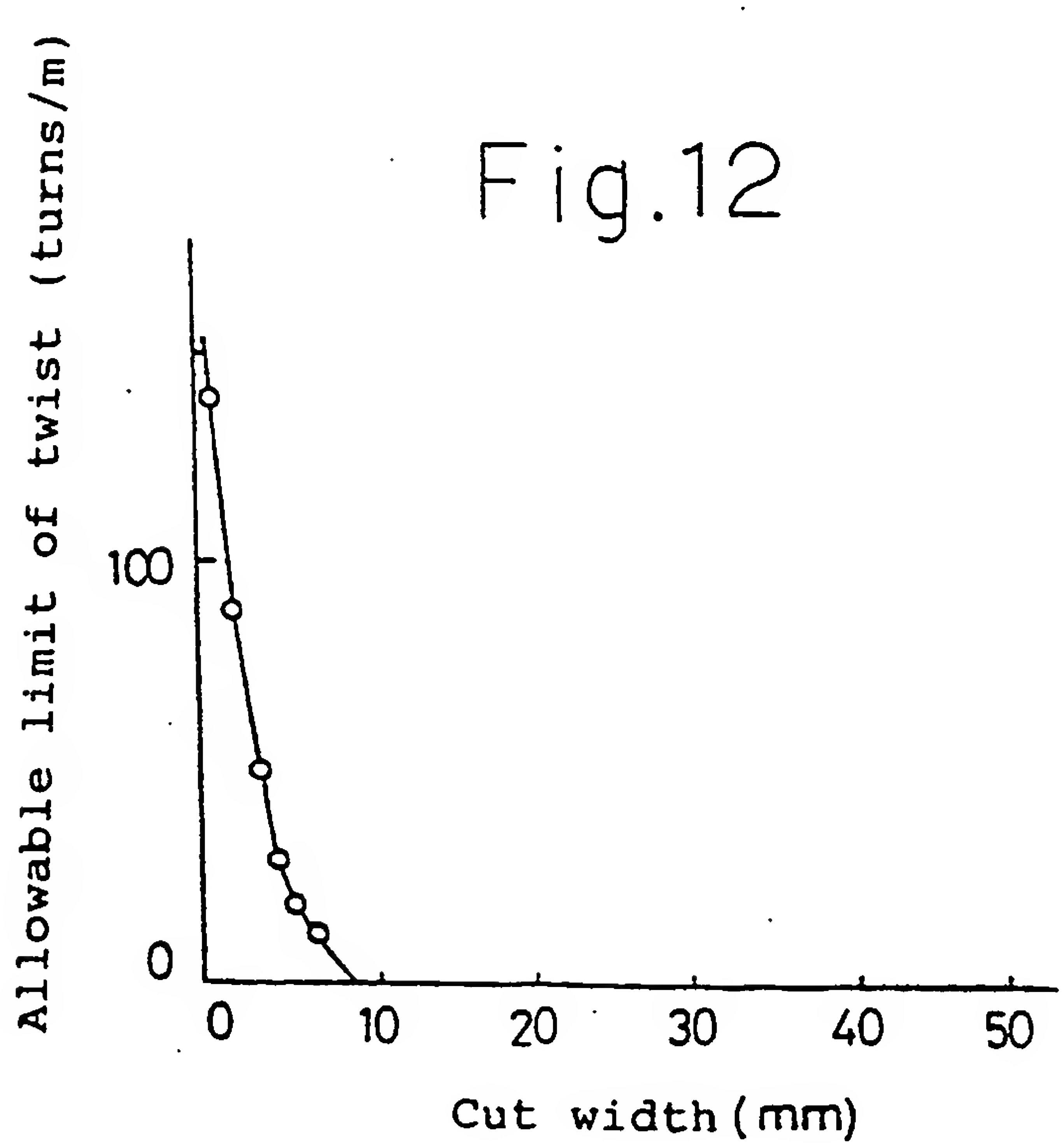

% Compressibility
50
0
0
10
20
30
40
50
Cut width (mm)

Fig.12


Allowable limit of twist (turns/m)
100
0
0
10
20
30
40
50
Cut width (mm)

PACKING MATERIAL AND PACKING MADE OF THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to packing material and packing preferably suitable to gland packing or the like for use in a shaft seal part of a hydraulic machine.

2. Prior Art

A variety of gland packings in which flexible graphite is used as a base material have been hitherto known for use in a shaft seal part or the like portion of a hydraulic machine, for example.

Gland packings of this sort are manufactured by various techniques, such as laminating, die molding, chip molding, and ribbon packing. However, these techniques require that the graphite material must be previously molded into a ring shape conforming to the diametral size of a shaft with which such packing is to be used; as such, the packing cannot be used with any shaft having a different diameter. Therefore, such packing lacks versatility in use. Another, difficulty with such packing is that since flexible graphite is of low tensile strength and brittle in itself, once the packing is mounted in position it is extremely difficult to remove same when replacement is required, which means less usability.

Further, the aforesaid manufacturing techniques individually have drawbacks of their own. The laminating technique involves the problem of poor yield, which leads to higher cost. Where the die molding or chip molding technique is employed, dies or metal molds are required, which means higher cost, and the packing produced is less versatile. The ribbon packing technique does not provide good workability. These difficulties may be overcome by forming the flexible graphite into a cord-like structure so that it may be used by being cut to a specified length conforming to the diameter of the shaft, as is the case with such other type of packing as fiber braided or knitted; but the trouble is that flexible graphite cannot be braided or knitted because, as pointed out above, it is in itself of low tensile strength and so brittle that its compressibility and allowable limit of twist are both extremely low. Therefore, it has hitherto been considered impossible to use such packing in such a way as is usual with the aforesaid fiber braided or knitted type of packing, that is, in such a way that the braided or knitted packing is cut to a length according to the diametral size of the shaft with which it is to be used, the so cut packing being then wound about the outer periphery of the shaft.

SUMMARY OF THE INVENTION

In order to overcome the aforesaid difficulties it is hence a primary object of this invention to present a packing material which can be either twisted or braided, and a twisted or braided cord-like packing by using the same packing material, by using a flexible graphite sheet cut to a width of less than 5 mm in order to advantageously utilize a characteristic feature of flexible graphite in sheet form in particular that if such sheet is cut to a width of less than 5 mm, both its compressibility and its allowable limit of twist are significantly increased as shown in FIG. 11 and FIG. 12, and by covering the flexible graphite sheet with a fiber material in order to attain the synergistic action of the fiber material and flexible graphite sheet.

It is a second object of this invention to present a packing material which can be either twisted or braided and is small in elongation and high in strength, and a twisted or braided cord-like packing by using the same packing material, by using a flexible graphite sheet cut to a width of less than 5 mm, laminating this flexible graphite sheet with at least one of reinforcing fiber material or foil material, and covering this surface with the fiber material to attain the synergistic action of the fiber material and flexible graphite sheet, and the reinforcing fiber or foil material.

It is a third object of this invention to present a packing material which can be either twisted or braided, and a twisted or braided cord-like packing by using the same packing material, by forming a bar mainly composed of flexible graphite particles and containing at least one of short fiber, rubber, resin or lubricant, and covering this surface with fiber in order to attain the synergistic action of the fiber material and the bar.

It is thus intended to improve the usability and versatility.

In the packing material of this invention, since a flexible graphite sheet cut to a width of less than 5 mm is used, the compressibility and the allowable limit of twist are increased to make it possible to twist or braid, and moreover since the surface is covered with fibers, the toughness against bending and sliding may be also enhanced.

Furthermore, when a flexible graphite sheet cut to a width of less than 5 mm is laminated with at least one of reinforcing fiber or foil material, the strength is further increased and the elongation is decreased. By covering this surface with the fiber, moreover, the toughness against bending or sliding may be improved.

Meanwhile, by forming a bar by using flexible graphite particles as the base material and containing at least one of short fiber, rubber, resin or lubricant, twisting or braiding is enabled, and by adding at least one of short fiber, rubber and resin to the base material mainly composed of flexible graphite particles, the strength is increased and the elongation is restricted. When the surface is further covered with fiber, the toughness against bending or sliding may be improved.

Therefore, any of the these packing materials permits a cord-like structure to be cut to a specified length conforming to the shaft diameter, which was impossible hitherto, and to be used as a gland packing by bending this cut cord-like structure in a ring form, so that the usability and versatility may be greatly enhanced.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially cutaway view in perspective showing one embodiment of the packing material of the invention;

FIG. 2 is a partially cutaway view in perspective showing a cord-like packing formed by square braiding eight knitting threads by using the packing material in FIG. 1;

FIG. 3 is a partially cutaway view in perspective showing a twisted cord-like packing formed by bundling a plurality of the packing material in FIG. 1;

FIG. 4 is a partially cutaway view in perspective showing another embodiment of the packing material of the invention;

FIG. 5 is a partially cutaway view in perspective showing a cord-like packing formed by square braiding

eight knitting threads by using the packing material in FIG. 4;

FIG. 6 is a partially cutaway view in perspective showing a twisted cord-like packing formed by bundling a plurality of the packing material in FIG. 4;

FIG. 7 is a partially cutaway view in perspective showing a modified example of the packing material of the invention;

FIG. 8 is a partially cutaway view in perspective showing a cord-like packing formed by square braiding eight knitting threads by using the packing material in FIG. 7;

FIG. 9 is a partially cutaway view in perspective showing a twisted cord-like packing formed by bundling a plurality of the packing material in FIG. 7;

FIG. 10 is a partially cutaway view in perspective showing another embodiment of the packing material having a bar-shaped core material of the invention;

FIG. 11 is a graph showing the relationship between flexible graphite sheet cut width and its compressibility; and

FIG. 12 is a graph showing the relationship between flexible graphite sheet cut width and its allowable limit of twist.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, the present invention is described in details below.

In FIG. 1, of the flexible graphite sheets less than 1 mm in thickness and less than 5 mm in width, six pieces of the most preferable flexible graphite sheet **1** measuring 0.38 mm in thickness and 3 mm in width are prepared, and the surface of these six flexible graphite sheets **1** is covered with knitted Aramid fiber or nickel-chromium-iron alloy fiber to form a knitting thread **4**, and this knitting thread **4** is used as the packing material.

FIG. 2 shows a cord-like packing, in which eight knitting threads **4** shown above are used, and are square braided to form a cord-like structure **5**, and the surface of the knitting threads **4**, that is, the surface of the knitted covering fibers is impregnated with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE (polytetrafluoroethylene) instead of rubber-based adhesive), or with preferably these three sealers **6** together with zinc or sodium nitrite as a corrosion preventive.

The packing in FIG. 3 is manufactured by bundling six knitting threads 4 and roll forming while twisting 20 turns/m to form a cord-like structure **5**, and impregnating the surface of the knitting threads **4**, that is, the surface of the knitted covering fibers with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers **6** together with zinc or sodium nitrite as a corrosion preventive.

FIG. 11 presents experimental results on the relationship between cut width and compressibility with respect to a flexible graphite sheet having a thickness of 0.38 mm, and FIG. 12 presents experimental results on the relationship between cut width and allowable limit of twist with respect to a 1-meter long flexible graphite sheet having a thickness of 0.38 mm.

It can be seen from these figures that the flexible graphite sheet has a characteristic feature that if its cut width is less than 5 mm, both its compressibility and its allowable limit of twist are remarkably increased.

This fact assures easy and accurate formation of a packing in a cord-like structure **5** as shown in FIG. 2 and FIG. 3, from the packing material (knitting thread **4**) having the surface of six flexible graphite sheets **1** cut to a width of less than 3 mm with knitted Aramid fibers or nickel chromium-iron alloy fibers. In other words, eight-thread square braiding and also twisting can be satisfactorily carried out without breakage being caused to the flexible graphite sheet **1** or the core material, that is, to the knitting thread **4**. Therefore, the cord-like structure **5** may be readily cut to a specified length conforming to the diameter of the shaft, for example, for use as a gland packing. This means improved usability and versatility.

In FIG. 4, of the flexible graphite sheets less than 1 mm in thickness and less than 5 mm in width, three pieces of the most preferable flexible graphite sheet **1** measuring 0.38 mm in thickness and 3 mm in width are prepared, and these three flexible graphite sheets **1**, and four lead foils **7** of 0.1 mm in thickness and 3 mm in width are alternately laminated to form a core **3**, and the surface of this core **3** is covered with knitted nickel-chromium-iron alloy fibers to form a knitting thread **4'**, which is used as the packing material.

FIG. 5 shows a cord-like packing, in which eight knitting threads **4'** shown above are used, and are square braided to form a cord-like structure **5'**, and the surface of knitting threads **4'**, that is, the surface of the knitted covering fibers is impregnated with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or with preferably these three sealers **6** together with zinc or sodium nitrite as a corrosion preventive.

The packing in FIG. 6 is manufactured by bundling six knitting threads **4'** and roll forming while twisting 20 turns/m to form a cord-like structure **5'**, and impregnating the surface of the knitting threads **4'**, that is, the surface of the knitted covering fibers with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers **6** together with zinc or sodium nitrite as a corrosion preventive.

Also from such packing material (knitting thread **4'**) manufactured by alternately laminating three flexible graphite sheets **1** cut to a width of 3 mm and four lead foils **7** to form a core **3**, and covering the surface of this core **3** with knitted nickel-chromium-alloy fibers, a packing in cord-like structure **5'** is obtained easilY and securely as shown in FIG. 5 and FIG. 6. In other words, an eight-thread square braiding and also twisting can be satisfactorily carried out without breakage being caused to the flexible graphite sheet **1** or the core material, that is, to the knitting thread **4'**. What is more, this knitting thread **4'** is remarkably increased in strength owing to the intervening existence of lamination of lead foil **7**, and since the surface is covered with knitting of nickel-chromium-iron alloy fibers, the bending performance is improved. Accordingly, the cord-like structure **5'** can be cut to a specified length conforming to, for example, the diameter of the shaft for use as a gland packing, which means improved usability and versatility.

FIG. 7 shows a modified example of the packing material in FIG. 4. Four flexible graphite sheets **1** of 0.38 mm in thickness are cut to a width of 3 mm, and a reinforcing fiber **2** made of 0.15 mmϕ nickel-chromium-iron alloy is laminated between the two layers in the top and bottom to form a core **3**, and the surface of this core **3** is covered with knitted 0.1 mmϕ INCONEL **600**

fibers to form a knitting thread 4'', which is used as the packing material.

FIG. 8 shows a cord-like packing, in which eight knitting threads 4'' shown above are square braided to form a cord-like structure 5'', and the surface of the knitting threads 4'', that is, the surface of knitted covering fibers is impregnated with at least one of silicone oil, scale-form graphite and rubberbased adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers 6 together with zinc or sodium nitrite as a corrosion preventive.

FIG. 9 shows a cord-like packing, in which six knitting threads 4'' are bundled, and are roll formed while twisting 20 turns/m to form a cord-like structure 5'', and the surface of the knitting threads 4'', that is, the surface of the knitted covering fibers is impregnated with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers 6 together with zinc or sodium nitrite as a corrosion preventive.

In FIG. 8 and FIG. 9, too, the cord-like structure 5'' can be easily and securely formed by the knitting thread 4'', and an eight-thread square braiding and twisting can be satisfactorily carried out without breakage being caused to the flexible graphite sheet 1 or the core material, that is, to the knitting thread 4''. Still more, the strength is remarkably increased by the reinforcing fiber 2 and knitted covering fiber (INCONEL 600), and the bending performance is also improved. Therefore, the cord-like structure 5'' can be cut to a specified length conforming to the diameter of the shaft, for example, so as to be used as a gland packing, which means improved versatility and usability.

FIG. 10 represents an example of the preparation of packing material, in which 60% flexible graphite particles, 25% natural graphite as lubricant, 10% rubber, and 5% Aramid short fibers are kneaded, and a circular solid bar-like structure 8 of 3 mmϕ is formed by an extrusion forming machine, and the surface of this bar-like structure 8 is covered with 0.1 mmϕ nickel-chromium-iron alloy fiber by knitting to form knitting thread 4''', which is used as the packing material.

From such packing material, that is, knitting thread 4''', a cord-like packing can be formed by square braiding eight knitting threads 4''', to form a cord-like structure the same as in FIG. 5, and by impregnating the surface of the knitting threads 4''' with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers 6 together with zinc or sodium nitrite as a corrosion preventive.

It is also possible to form a cord-like packing by bundling six knitting threads 4''', and roll forming while twisting by 20 turns/m to form a cord-like structure the same as in FIG. 6, and by impregnating the surface of the knitting threads 4''' with at least one of silicone oil, scale-form graphite and rubber-based adhesive (or PTFE instead of rubber-based adhesive), or preferably with these three sealers 6 together with zinc or sodium nitrite as a corrosion preventive.

In order words, even from the packing material (knitting thread 4''') as stated above, a cord-like packing can be formed easily and securely, and eight-thread square braiding or twisting of the knitting threads 4''' can be satisfactorily carried out without breakage being caused to the bar-like structure 8 mainly composed of flexible graphite particles or the core material, that is, to the knitting threads 4'''. Still more, since rubber and Aramid short fibers are kneaded, the strength is significantly increased, and the bending performance is improved, and this cord-like packing can be cut to a specified length conforming to the diameter of the shaft for use, for example, as a gland packing, which means improved versatility and usability.

As the reinforcing fiber 2 and covering fiber in the above embodiments, 0.1 mmϕ nickel-chromium-iron alloy is used, but it is not limitative, and other materials may be used depending on the purpose of such, for example, metal fibers such as MONEL and stainless steel, inorganic fibers such as asbestos, ceramic fiber, glass fiber and carbon fiber, and organic fibers such as cotton, rayon, phenol, Aramid, PBI (polybenzimidazole), PTFE (polytetrafluoroethylene), PEI (polyetherimide), PPS (polyphenylene sulfite), and PEEK (polyether etherketone).

As the foil material, 0.1 mm thick lead foil is used in the example, but metal foils such as copper and aluminum, pulse sheet, Aramid sheet, PBI sheet, PTFE sheet, PEI sheet, PSS sheet, PEEK sheet and others may be used depending on intended use.

As the short fiber to be kneaded with flexible graphite particles, in the above embodiment, Aramid short fiber was used, but it is not limitative, and other materials may be used depending on intended use, for example, metal short fibers such as nickel-chromium-iron alloy nickel-copper alloy and stainless steel, inorganic short fibers such as asbestos, ceramic fiber, glass and carbon, and organic short fibers such as cotton, rayon, phenol, Aramid, PBI, PTFE, PEI, PPS and PEEK. As the rubber, nitrile rubber, chloroprene rubber, fluororubber and others may be properly used selectively, and examples of resin may include, in particular, phenol resin and epoxy resin. As the lubricant, aside from the aforesaid natural graphite, expanded graphite, mica, petroleum wax and others may be used depending on intended use.

In the illustrated example, the solid bar-like structure 8 is formed by extruding a mixed material mainly composed of flexible graphite particles, but the bar-like structure 8 may be formed in a circular solid section by rounding a flexible graphite sheet of less than 5 mm in width, or a flexible graphite sheet cut in a rectangular form with width of less than 5 mm may be mixed together with at least one of short fiber, rubber and resin, and formed in a circular solid section.

In the above embodiments, the knitting threads 4, 4', 4'', 4''', are prepared by bundling a plurality of threads and twisting or braiding them, but it is also possible to compose a gland packing by twisting a single knitting thread 4, 4', 4'' or 4''' so as to be suited to the dimensions or composition of the shaft seal part.

Meanwhile, in the aforesaid embodiments, the knitting threads 4, 4', 4'', 4''' are square braided, but, of course, braiding by tubular plain stitch or lattice braiding may be used.

As the covering fiber, aside from the knitting shown above, tubular plain stitch, conduit knitting or tubular weaving may be applied, too.

The measured data of knitting threads are shown in Table 1.

TABLE 1

	Use in manufacture							
	Core		Surface covering		Properties		Processability	
No.	Material	Process	Material	Process	Strength kg	Elongation %	Twist	Braid
1	Corresponding to FIG. 1 of this invention	Laminate	Aramid (spun yarn) count 20	Knitting	4.5	15.8	Possible	Possible
2	Corresponding to FIG. 1 of this invention	"	nickel-chromium-iron alloy 600 0.1 mmϕ	"	5.7	10.0	Possible	Possible
3	Corresponding to FIG. 7 of this invention	"	nickel-chromium-iron alloy 600 0.1 mmϕ	"	7.2	5.3	Possible	Possible
4	Corresponding to FIG. 4 of this invention	"	nickel-chromium-iron alloy 600 0.1 mmϕ	"	5.0	9.2	Possible	Possible
5	Extrusion forming of flexible graphite powder 3 mmϕ	Extrusion	nickel-chromium-iron alloy 600 0.1 mmϕ	"	0.8	1.5	Impossible	Impossible
6	Corresponding to FIG. 10 of this invention	Kneading, extrusion	nickel-chromium iron alloy 600 0.1 mmϕ	"	3.8	4.1	Possible	Possible

As clear from Table 1, the packing materials No. 1, No. 2, No. 3, No. 4 and No. 6 of this invention, are higher in strength and smaller in elongation as compared with the packing material No. 5, and it is also known that twisting and braiding can be carried out satisfactorily.

In the above embodiments, it is explained that the knitting threads 4, 4', 4", 4"' are braided to be used as gland packing, but not limited to such gland packing, by ribbon stitching or plain stitching of knitting threads 4, 4', 4", 4"', it may be possibly applied as a sealing packing between static members, and in this case, too, the same action and effect as in fabrication of glad packing will be obtained.

Thus, in the packing material and packing according to this invention, being composed of flexible graphite, it is not necessary to make as many packings as the number of different dimensions of shaft seal members, and bending and toughness are improved, and it may be preferably used as the gland packing or sealing material of static members.

What is claimed is:

1. A packing material prepared by: cutting a flexible graphite sheet to a width of less than 5 mm; laminating the flexible graphite sheet and at least one of reinforcing fiber and foil material; and covering the surface of the laminated flexible graphite sheet with fibers.

2. A packing material as set forth in claim 1, wherein the reinforcing fiber comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzimidazole. polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

3. A packing material as set forth in claim 1, wherein the foil comprises a material selected from metallic foils including lead, copper and aluminum, or nonmetallic foils including pulp sheet, Aramid sheet, polytetrafluoroethylene sheet, polyetherimide sheet, polyphenylene sulfite sheet and polyether etherketone sheet.

4. A packing material as set forth in claim 2, wherein the covering fibers comprise a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, organic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylele sulfite and polyether etherketone.

5. A packing material as set forth in claim 3, wherein the covering fibers comprise a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, organic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzximidazole, polytetrafluoroethylene, polyetherimide, polyphenylele sulfite and polyether etherketone.

6. A packing material as set forth in claim 4, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

7. A packing material as set forth in claim 5, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

8. A packing material as set forth in claim 6, wherein the thickness of the flexible graphite sheet is less than 1 mm.

9. A packing material as set forth in claim 7, wherein the thickness of the flexible graphite sheet is less than 1 mm.

10. A packing material as set forth in claim 8, wherein one to ten flexible graphite sheets are used.

11. A packing material as set forth in claim 9, wherein one to ten flexible graphite sheets are used.

12. A packing material as set forth in claim 11, wherein the flexible graphite sheets and foil materials are laminated alternately.

13. A packing material as set forth in any one of claims 6, 7, 8, 9, 10, 11, or 12, wherein the surface of the covering fibers is impregnated with one or graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene as a surface treatment agent.

14. A packing material as set forth in any one of claims 6, 7, 8, 9, 10, 11, or 12, wherein the surface of the covering fibers is impregnated with one of graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene as a surface treatment agent, and any one of zinc and sodium nitrite as a corrosion preventive.

15. A packing, fabricated by: cutting flexible graphite sheets to a width of less than 5 mm; laminating the flexible graphite sheets and at least one of reinforcing fiber and foil material, covering the surface of the laminated flexible graphite sheets with fibers; impregnating the surface of the covering fibers with a surface treat-

ment agent to obtain a packing material, which is twisted or braided.

16. A packing as set forth in claim 15, wherein the reinforcing fiber comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

17. A packing as set forth in claim 15, wherein the foil comprises a material selected from metallic foils including lead, copper, and aluminum, or nonmetallic foils including pulp sheet, Aramid sheet, polytetrafluoroethylene sheet, polyetherimide sheet, polyphenylene sulfite sheet and polyether etherketone sheet.

18. A packing as set forth in claim 16, wherein the covering fibers comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, organic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybezimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

19. A packing as set forth in claim 17, wherein the reinforcing fiber comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

20. A packing as set forth in claim 18, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

21. A packing as set forth in claim 19, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

22. A packing as set forth in claim 20, wherein the thickness of the flexible graphite sheet is less than 1 mm.

23. A packing as set forth in claim 21, wherein the thickness of the flexible graphite sheet is less than 1 mm.

24. A packing as set forth in claim 22, wherein one to ten flexible graphite sheets are used.

25. A packing as set forth in claim 23, wherein one to ten flexible graphite sheets are used.

26. A packing as set forth in claim 25, wherein the flexible graphite sheets and foil materials are laminated alternately.

27. A packing as set forth in claim 24, wherein at least one packing is twisted into a cord.

28. A packing as set forth in claim 25, wherein at least one packing is twisted into a cord.

29. A packing as set forth in claim 24, wherein said packing is formed in a cord by any one of square braiding tubular plain stitching, lattice knitting, ribbon weaving, and plain stitching and braiding.

30. A packing as set forth in claim 25, wherein said packing is formed in a cord by any one of square braiding, tubular plain stitching, lattice knitting, ribbon weaving, and plain stitching and braiding.

31. A packing as set forth in claim 26, wherein said packing is formed in a cord by any one of square braiding, tubular plain stitching, lattice knitting, ribbon weaving, and plain stitching and braiding.

32. A packing as set forth in any one of claims 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30 or 31, wherein any one of graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene is used as a surface treatment agent.

33. A packing as set forth in any one of claims 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, or 31, wherein any one of graphite powder, silicone oil, rubber-based adhesive polytetrafluoroethylene is used as a surface treatment agent, and any one of zinc and sodium nitrite is used as a corrosion preventive.

34. A packing material prepared by: impregnating the principal component of flexible graphite particles with at least one of short fiber, rubber, resin or lubricant to form a bar-like structure; and coating the surface of the impregnated flexible graphite particles with covering fibers.

35. A packing material as set forth in claim 34, wherein the short fiber is selected from metal short fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic short fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, or organic short fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone, the rubber is selected from nitrile rubber, chloroprene rubber or fluororubber, the resin is selected from phenol resin and epoxy resin, and the lubricant is selected from natural graphite, expanded graphite, mica and petroleum wax.

36. A packing material as set forth in claim 35, wherein the covering fiber comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless, steel, inorganic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

37. A packing material as set forth in claim 36, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

38. A packing material as set forth in claim 37, wherein the surface of the covering fibers is impregnated with one of graphite powder, silicone oil, rubber-based adhesive polytetrafluoroethylene as a surface treatment agent.

39. A packing material as set forth in claim 37, wherein the surface of the covering fibers is impregnated with one of graphite powder, silicone oil, rubber-based adhesive polytetrafluoroethylene, and at least one of zinc and sodium nitrite as a corrosion preventive.

40. A packing material as set forth in anyone of claims 34, 35, 36, 37, 38, or 39, wherein the bar-like structure is solid and circular in section.

41. A packing, fabricated by: impregnating the principal component of flexible graphite particles with at least one of short fiber, rubber, resin or lubricant to form a bar-like structure; coating the surface of the impregnated flexible graphite particles with fibers; and impregnating the surface of the covering fibers with a surface treatment agent to form a packing material, which is twisted or braided.

42. A packing material as set forth in claim 41, wherein the short fiber is selected from metal short fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic short fibers

including asbestos, ceramics fiber, glass fiber and carbon fiber, or organic short fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone, the rubber is selected from nitrile rubber, chloroprene rubber or fluororubber, the resin is selected from phenol resin and epoxy resin, and the lubricant is selected from natural graphite, expanded graphite, mica and petroleum wax.

43. A packing material as set forth in claim **42**, wherein the covering fiber comprises a material selected from metal fibers including nickel-chromium-iron alloy, nickel-copper alloy and stainless steel, inorganic fibers including asbestos, ceramics fiber, glass fiber and carbon fiber, and organic fibers including cotton, rayon, phenol, Aramid, polybenzimidazole, polytetrafluoroethylene, polyetherimide, polyphenylene sulfite and polyether etherketone.

44. A packing material as set forth in claim **43**, wherein the covering fibers are knitted by any one of, tubular plain stitched, conduit knitted, and tubular woven.

45. A packing as set forth in claim **44**, wherein at least one packing is formed into a cord by twisting.

46. A packing as set forth in claim **44**, wherein at least one packing is formed into a cord by any one of square braiding, tubular plain stitching, lattice knitting, ribbon weaving, plain stitching and braiding.

47. A packing as set forth in claim **45**, wherein any one of graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene is used as surface treatment agent.

48. A packing as set forth in claim **46**, wherein any one of graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene is used as a surface treatment agent.

49. A packing as set forth in claim **45**, wherein any one of graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene is used as a surface treatment agent, and any one of zinc and sodium nitrite is used as a corrosion preventive.

50. A packing as set forth in claim **46**, wherein any one graphite powder, silicone oil, rubber-based adhesive and polytetrafluoroethylene is used as a surface treatment agent, and any one of zinc and sodium nitrite is used as a corrosion preventive.

51. A packing material as set forth in any one of claims **41**, **42**, **43**, **44**, **45**, **46**, **47**, **48**, **49**, or **50**, wherein the bar-like structure is solid and circular in section.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,134,030

DATED : July 28, 1992

INVENTOR(S) : Takahisa Ueda et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claim 2, column 7, line 54, "." should be ",".

Claim 4, column 8, line 22, "polyphenylele" should be "polyphenylene".

Claim 5, column 8, line 30, "polybenzximidazole" should be "polybenzimidazole"; and
line 31, "polyphenylele" should be "polyphenylene".

Claim 13, column 8, line 54, "or" should be "of".

Claim 15, column 8, line 67, "and" should be inserted between the ";" and "impregnating".

Claim 18, column 9, line 24, "polybezimidazole" should be "polybenzimidazole".

Claim 36, column 10, line 34, the "," (second occurrence) should be deleted.

Claim 40, column 10, line 54, a blank space should be inserted between "any" and "one".

Claim 47, column 12, line 7, "a" should be inserted between "as" and "surface"

Claim 50, column 12, line 19, "of" should be inserted between "one" and "graphite".

Signed and Sealed this

Fourteenth Day of September, 1993

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer — *Commissioner of Patents and Trademarks*

APPENDIX C – RELATED PROCEEDINGS

None